A. WERNER. ANN 375, 1 (1910)

UBER MEHRKERNIGE HEJALLAMMONIAKE

ON POLYNUCLEAR METAL-AMMINES

by A. Werner

from

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Translated by

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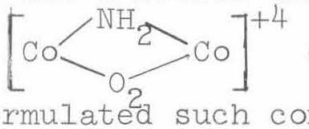
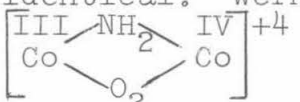
Translator's Notes

The nomenclature used by Werner has been modified and updated as much as possible to more clearly indicate which compounds were being studied.

The reader is strongly recommended to use the latest review in the field of binuclear cobalt complexes by A. G. Sykes and J. A. Weil (Progress in Inorganic Chemistry, Volume 14; J. O. Edwards, ed.; Interscience, Wiley and Sons Publishers, 1970) as a companion reference to this translation. This review contains the most comprehensive bibliography of work in the field and also a listing of all other reviews published prior to July 1969.

No attempt has been made to correct Werner's chemistry, e.g., it is now well established that the electron density on the cobalt atoms in $[CoO_2Co]^{+5}$ and  complexes is identical. Werner, however, formulated such complexes as  because he assumed that the O_2 group was a peroxide group rather than a superoxide group. Werner's original formulations have been followed throughout the paper. Formulations that have been disproven in the time since Werner completed his work are translated without correction but are accompanied by a dagger (†). Translator's notes in the text appear as footnotes using asterisks (*).

Obvious typographical and typesetting errors have been corrected throughout the paper. Oxidation states of metals have been included in the formulations as Roman numerals, e.g.

"Octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate"

which, in this case, indicates that Werner has formulated the nucleus as having one trivalent and one tetravalent cobalt.

Page numbers from the original appear in the right margin in brackets, so that text in the translation may be easily referenced to the original.

Acknowledgments

I wish to express my deepest thanks and appreciation to Dr. John A. Weil of Argonne National Laboratory for his aid, encouragement and guidance in preparing the final draft of this translation. I would also like to thank Dr. Paul Bowerman, Dr. Richard E. Marsh, and Dr. William P. Schaefer for their kind advice and assistance. My thanks also go to Diane Morgan and Cathy Carbaugh who typed the final draft. I am grateful for the use of some of the facilities of Argonne National Laboratory which greatly aided the completion of this work.

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ON POLYNUCLEAR METAL-AMMINES

by A. Werner

[Part 10] [1]

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[1]Earlier Parts: 1. Zeitschr. f. anorg. Chem. (1898) 16:109; 2. Ibid. (1899) 21:96; 3. Ber. d. d. chem Ges. (1907) 40:2103; 4. Ibid. (1907) 40:4426; 5. Ibid. (1907) 40:4434; 6. Ibid. (1907) 40:4605; 7. Ibid. (1907) 40:4834; 8. Ibid. (1908) 41:3879; 9. Ibid. (1908) 41:3912.

(received June 2, 1910)

THE CONSTITUTION OF POLYNUCLEAR COBALT-AMMINES

Our research of many years on polynuclear metal-ammines is now complete insofar as there can be no more doubt as to the constitution of the more thoroughly investigated series of compounds. The following therefore begins with a summary of the results of these investigations and will then report that part of the extensive experimental information which has up to now been unpublished or is available only in dissertations.

This paper deals primarily with the polynuclear cobalt ammines, the research upon which has advanced the furthest.

The clarification of the constitution of these singular compounds was particularly difficult because it was first necessary to understand new kinds of bonding, differing from those already observed, occurring with certain atoms and groups of atoms possessing this capability. After this was accomplished, however, the picture of the constitution of the polynuclear cobalt ammines became more self-consistent with each new investigation. New relations between the different series could be proven and, on the basis of these relations, completely different series were successfully converted from one into the other, thus making possible other, further checks on independently derived representations for the constitutions of different series. [2]

As a result of this, a theory of the constitution of polynuclear inorganic compounds has developed which represents a substantial further development in the theory of coordination compounds and which furnishes a more reliable basis for the interpretation of the constitution of large groups of widely different inorganic compounds.

The following, some as Doctoral candidates and some as assistants, have taken part in these investigations: Mssrs. F. Beddow, A. Baselli, A. Mylius, K. Rücker, F. Steinitzer, A. Grün, E. Bindschedler, E. Berl, F. Salzer, M. Rappaport, M. Pieper, G. Jautsch, O. deVries, A. Schaarschmidt, E. Welti, J. Dubsky, J. Fürstenberg, J. Posselt, J. Rapiport, Aig. Tschudi, M. Feinberg, E. Schelze, Miss S. Malmgren and Miss H. Grigorieff. The aid of my co-workers in the experimental work has been especially appreciated.

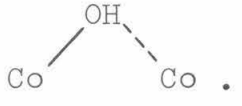
I. General results of the investigations

The most important results of the study of polynuclear cobalt ammines are related on one hand to the theory of valence, specifically the theory of the bond-forming capabilities of elementary atoms, and on the other hand to the theory of isomeric phenomena.

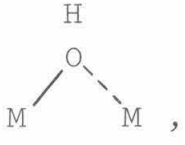
A. Valence theoretical results [3]

The bond formation capabilities of atoms that have been incontestably established by the experimental data and which seem of importance to the theory of atomic valence are described below.

1. The oxygen of a hydroxyl group bonded to a cobalt atom has the capability of forming a bond to another cobalt atom in the sense of the following diagram:



This ability to participate structurally in the formation of another stable bond has been substantiated in numerous cases where a hydroxyl group is bonded to a cobalt atom and also occurs for hydroxyl groups bonded to other metals. This has been demonstrated in the case of chromium, for example, by P. Pfeiffer. This proven possibility that two metal atoms can be bound together by a hydroxyl group,



is of fundamental importance in evaluating the constitution of

basic metal salts, as I have emphasized previously[1] and will

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[1]Ber. d. d. chem. Ges. (1907), 40:4441

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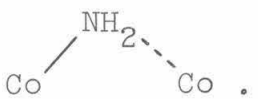
develop more thoroughly in a later paper. This capability is also of importance as it demonstrates that oxygen frequently participates structurally with three valences (two primary valences and one secondary valence).

2. The nitrogen of an amide group which is bonded to a cobalt atom possesses the property of being able to form a stable bond to a second cobalt atom, according to the following diagram:



This linking of two cobalt atoms to one another through an amido group is very stable and plays a primary role in the formation of polynuclear cobalt ammines.

3. An oxygen molecule is capable of serving as the [4]
bridge between two cobalt atoms, namely, between two trivalent cobalt atoms

$$Co(III) - O_2 - Co(III)$$

or between one trivalent and one tetravalent cobalt,

$$Co(IV) - O_2 - Co(III) \ .$$

It must be emphasized that this tendency, for cobalt to form complexes in which one trivalent and one tetravalent cobalt atom

are connected by an oxygen molecule, is particularly striking. Of the five products of the air oxidation of ammoniacal cobalt salt solutions shown to be polynuclear cobalt ammines, no less than three exhibit this remarkable combination of atoms.

4. In no case are the two cobalt atoms in a polynuclear cobalt-ammine bonded directly to one another; rather, they are always linked to each other through the interposition of another element.

5. When two cobalt atoms are bound to one another by OH^- or NH_2^-, they can contain the following additional bridging groups: NO_2^-, $SO_4^{=}$, CH_3COO^-, $RCOO^-$, $C_2O_4^{=}$.

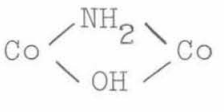
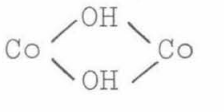
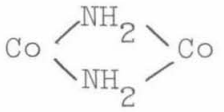
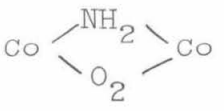
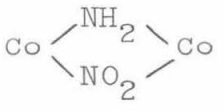
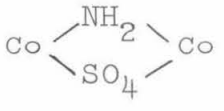
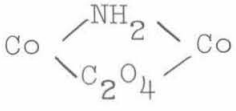
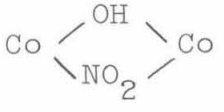
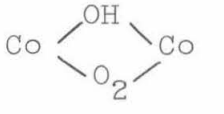
6. Two cobalt atoms can be bound together by one, two, or three bridging groups. As of this time, the following combinations have been characterized with certainty.

a. Binuclear cobalt-ammines

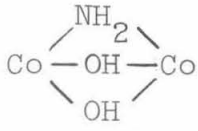
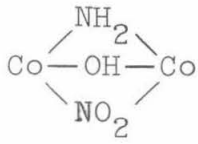
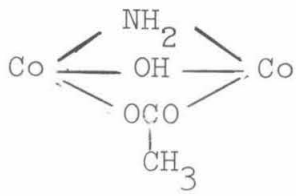
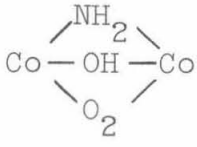
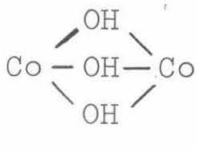
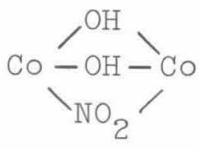
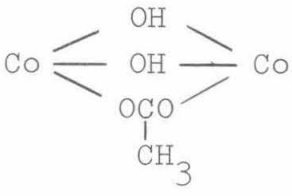
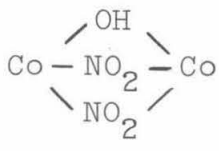
1) with one bridge:

$Co-NH_2-Co$, $Co^{III}-O_2-Co^{III}$, $Co^{IV}-O_2-Co^{III}$

2) with two bridges:

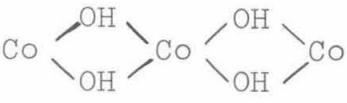










3) with three bridges: [5]

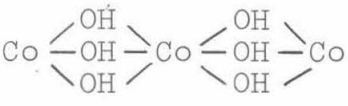









b. Trinuclear cobalt-ammines

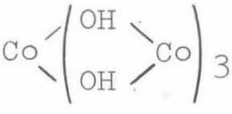
1) with four bridges



2) with six bridges



c. Tetranuclear cobalt-ammines with six bridges



We have now established the existence of twenty-three different molecular species of polynuclear cobalt-ammines.

The fact that more than three bridges between two cobalt atoms could not be found can be simply explained, since, if the six groups about the cobalt are considered to be in an octahedral configuration, then two octahedra can possess at most three corner points in common.

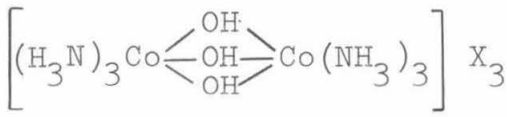
7. In all of the compounds investigated, the maximum coordination number of the trivalent and tetravalent cobalt is six, i.e., the coordination number has the same maximum value as in the simple cobalt-ammines.

B. New results relating to inorganic isomerism [6]

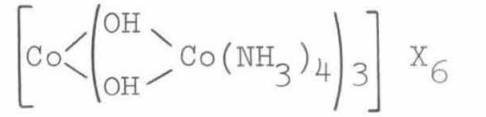
The following must be emphasized regarding the new isomeric phenomena: Three new types of isomerism have been observed in polynuclear cobalt ammines, namely: 1) a new type of polymerism, which I wish to call "nuclear polymerism," 2) a theoretically very interesting type of "valence polymerism," and 3) a type designated "coordinative structural isomerism."

For an understanding of the nature of these new kinds of isomerism we will be best able to orient ourselves with the aid of the constitutional formulas of the isomers:

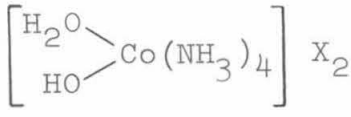
1. Polymerism



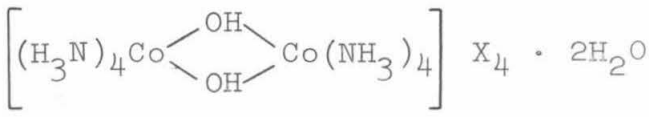
Hexammine tri-μ-hydroxo dicobalt(III) salts



Dedecammine-hexa-μ-hydroxo tetracobalt(III) salts



Hydroxoaquotetrammine cobalt(III) salts



Octammine-di-μ-hydroxo dicobalt(III) salts

As can be seen from these formulas, we are dealing with isomeric phenomena that are a consequence of a polymerization of complex cations. In order to differentiate this polymerism from the thoroughly characterized coordination polymerism, we denote this as "nuclear polymerism."

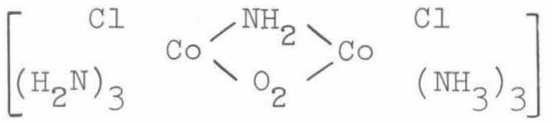
2. Valence isomerism

Tetraethylenediamine-μ-amido-μ-peroxo dicobalt (III,IV) salts

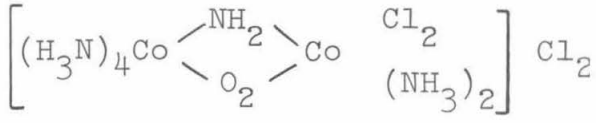
Tetraethylenediamine-μ-ammonium-μ-peroxo dicobalt (III,IV) salts

These isomeric compounds differ from one another in that, in the first case, the bridging nitrogen is bonded to one cobalt [7] atom through a primary valence, to the other cobalt atom through a secondary valence, and to the two hydrogen atoms through primary valences, while in the second case the bridging nitrogen is bonded to both cobalt atoms and one hydrogen atom through primary valences, but to the second hydrogen atom through a secondary valence. Insofar as the configuration of the cation's ligands are concerned, the salts of these two series do not differ constitutionally, but rather only in the special valences which are involved in the bonding. The salts of the first series are green and form neutral solutions; the salts of the second are red and form acidic solutions.

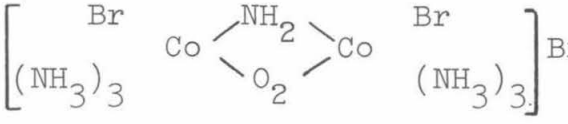
3. Coordinative structural isomerism



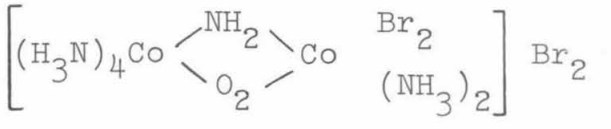
Symdibromohexammine-μ-amido-μ-peroxo dicobalt (III,IV) bromide



Asymdichlorohexammine-μ-amido-μ-peroxo dicobalt (III,IV) chloride

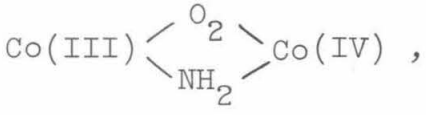


Symdibromohexammine-μ-amido-μ-peroxo dicobalt (III,IV) bromide



Asymdibromohexammine-μ-amido-μ-peroxo dicobalt (III,IV) bromide

As can be seen from these formulas, these isomeric series which possess the same molecular nucleus,



differ in how the six ammonia molecules and the two directly bonded halogen atoms are distributed about the two cobalt atoms. In the one case, the six ammonia molecules and the two halogen atoms are symmetrically distributed (3:3 and 1:1) on the two cobalt atoms, while in the second case the distribution is asymmetrical (4:2 and 2:0).

These isomers can be compared with isomers of organic [8] compounds of the form:

i.e., with the substitutional isomers or structural isomers that abound in organic chemistry. For this reason I would like to propose that this isomerism be called coordinative structural isomerism.

Both series of salts are deep green in color, differing only slightly in appearance. In contrast to this, their chemical properties are quite different from one another.

II. Determination of the constitution of the polynuclear cobalt-ammines

A. Decammine-μ-amido dicobalt(III) salts[1]

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[1]Ber. d. d. Chem. Ges. (1908) 41:3912

$$[(H_3N)_5Co\text{-}NH_2\cdots Co(NH_3)_5]X_5 \ .$$

The decammine-μ-amido dicobalt(III) salts have been synthesized from the octammine-μ-amido dicobalt(III) salts* by the addition of

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*Translator's note: This is probably a manuscript error. Werner probably meant the octammine-μ-amido-μ-hydroxo dicobalt (III) salts.

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ammonia. Of the polynuclear ammines possessing one amido bridging group they are the richest in ammonia, and are notable for their splendid, delicate bluish-red color and the fine silky luster of their crystals. All normal salts of the decammine series form neutral solutions.

The way these salts decompose in mineral acids is of utmost importance in the evaluation of their constitution. Long digestion in a mixture of hydrochloric and sulfuric acids in a water bath cleaves them smoothly into chloropentammine cobalt(III) salts and hexammine cobalt(III) salts. This result permits only one possible distribution of the ammonia molecules about the two cobalt atoms, as is apparent from the formulation:

$$[(H_3N)_5Co\text{-}NH_2\text{-}Co(NH_3)_5]Cl_5 + HCl \rightarrow [(H_3N)_6Co]Cl_3 + \left[Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]Cl_2 .$$

The general structure of the complex radical cannot be doubted, the remaining question being which of the two structures below is best: [9]

$$[(H_3N)_5Co\text{-}NH_2\cdots Co(NH_3)_5]\,X_5 \quad \text{or} \quad [(H_3N)_5Co\text{-}\underset{\vdots}{\underset{HX}{NH}}\text{-}Co(NH_3)_5]\,X_4 .$$

This question is not without basis, for isomers have been found in other series which have constitutional differences of this kind. Observations on such isomers have shown, however, that compounds corresponding to the first formula must form neutral solutions, while solutions of those corresponding to the second must be acidic. Since the salts of our decammine series are neutral, they must correspond to the first of the above two constitutional formulas.

B. Oxycobalt ammines and anhydro-oxycobalt ammines[1,*]

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[1]Zeitschr. f. anorg. Chem. (1898) 16:245

*Translator's note: These are synonyms for what are now known to be the μ-peroxo bis{Co(III) L_5} salts and the μ-superoxo bis{Co(III) L_5} salts, L representing a monodentate ligand.

$[(H_3N)_5Co\text{-}O_2\text{-}Co(NH_3)_5]\ X_4$ and $[(H_3N)_5Co\text{-}O_2\text{-}Co(NH_3)_5]\ X_5$.

These two series of compounds are closely related to one another in that the anhydro-oxycobalt ammines are formed from the oxycobalt ammines.

The constitution of the two series was clarified long ago through an investigation carried out jointly by A. Mylius and myself. The oxycobalt ammines are the primary oxidation products formed whenever ammoniacal solutions of cobalt salts are subjected to air oxidation. They have a brown-black color, whereas the anhydro-oxycobalt ammine salts are a deep green.

C. Octammine-μ-amido-μ-hydroxo dicobalt(III) salts

$$\left[(H_3N)_4Co\begin{matrix}\diagup NH_2 \diagdown \\ \diagdown OH \diagup\end{matrix}Co(NH_3)_4\right] X_4 .$$

The sulfate of this series is the main constituent of the so-called Vortmann's Sulfate. The preparation of the latter [10]
and its conversion into octammine-μ-amido-μ-hydroxo dicobalt(III) salts has already been described.[1]

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[1]Ber. d. d. Chem. Ges. (1907) 40:4605

That the octammine-μ-amido-μ-hydroxo dicobalt(III) salts can be converted into decammine-μ-amido dicobalt(III) salts may be cited as proof that an amido group serves as a bridge between the two cobalt atoms in the former. This conversion is effected by treating octammine-μ-amido-μ-hydroxo dicobalt(III) nitrate with concentrated nitric acid, giving the nitrate of the nitratoaquo-octammine-μ-amido dicobalt(III) series:[2]

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[2]Ber. d. d. Chem. Ges. (1908) 41:3914

$$\left[(H_3N)_4Co\begin{matrix}OH\\NH_2\end{matrix}Co(NH_3)_4\right](NO_3)_4 + HNO_3 = \left[\begin{matrix}O_3N\\(H_3N)_4\end{matrix}Co\text{-}NH_2\text{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right](NO_3)_4 \cdot$$

Very good yields of the decammine nitrate are obtained by reaction of the latter salt with liquid ammonia:

$$\left[\begin{matrix}O_3N\\(H_3N)_4\end{matrix}Co\text{-}NH_2\text{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right](NO_3)_4 + 2NH_3 =$$

$$H_2O + [(H_3N)_5Co\text{-}NH_2\text{-}Co(NH_3)_5](NO_3)_5 \cdot$$

This conversion may also be achieved by treating chloronitrato-octammine-μ-amido dicobalt(III) nitrate with liquid ammonia:

$$\left[\begin{matrix}Cl\\(H_3N)_4\end{matrix}Co\text{-}NH_2\text{-}Co\begin{matrix}NO_3\\(NH_3)_4\end{matrix}\right](NO_3)_3 + 2NH_3 = \left[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_5\right]\begin{matrix}Cl\\(NO_3)_4\end{matrix} \cdot$$

The procedure for carrying out this reaction will be described in detail in the experimental section.

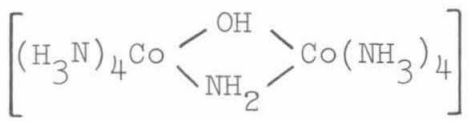
In addition to the amido bridge, a hydroxo bridge is assumed to be situated between the two cobalt atoms in the octammine salts. The proof for this assumption is as follows: The octammine-μ-amido-μ-hydroxo salts correspond to the general formula:

$$\left[(H_3N)_8Co_2 \begin{matrix} NH_2 \\ OH \end{matrix}\right] X_4 \ ,$$

and consequently contain a hydroxyl group bonded to a cobalt. [11] This hydroxyl group, however, cannot have the same function as the hydroxyl group in the hydroxo cobalt ammines (which I have also thoroughly investigated), because hydroxyls of this type cause the compounds concerned to act as bases, as is indicated, for example, by the behavior of hydroxo pentammine cobalt salts, $Co\left[\begin{matrix} OH \\ (NH_3)_5 \end{matrix}\right] X_2$. The salts of our series, however, form completely neutral solutions. The secondary valence of the hydroxy group, which causes the alkaline reaction by bonding to hydrogen ions in the water, must already be satisfied in these compounds. There is only one possible way that this can occur, as is evident from the formula:

$$\left[(H_3N)_4Co \begin{matrix} OH \\ NH_2 \end{matrix} Co(NH_3)_4\right] X_4 \ .$$

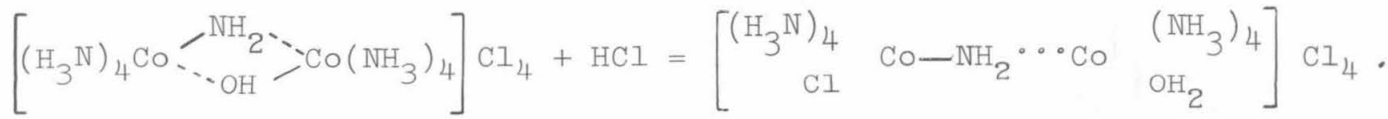
The hydroxyl group must fill the remaining available coordination vacancy on the second cobalt atom, thus saturating its secondary valence by binding to that cobalt atom. This leads us to the following formula:



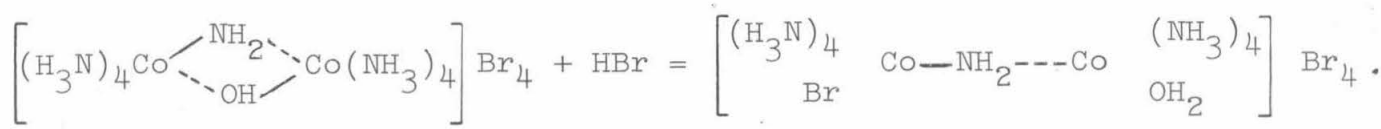
This formula is consistent with the synthesis and the behavior of the salts of this series to such a degree that its validity cannot be doubted, as will also be evident from the subsequent discussion.

It is characteristic of the octammine-μ-amido-μ-hydroxo dicobalt(III) series that its hydroxo bridge is easily split off by acids; the amido bridge, however, appears to be much more resistant, being cleaved only by much longer and more vigorous attack by concentrated acids. Those reactions leading to the destruction of the amido bridge are of special interest in the determination of the constitution, whereas the reactions in which only the hydroxo bridge is destroyed lead to various new series of compounds. [12]

Up to now we have investigated the reaction products of this series with the following acids: hydrochloric, hydrobromic, nitric, sulfuric, oxalic and nitrous. Reaction with the first three acids, due to the loss of the hydroxo bridge, generates compounds whose formation reactions follow the equations below:



Chloroaquooctammine-μ-amido dicobalt(III) salts



Bromoaquooctammine-μ-amido dicobalt(III) salts

$$\left[(H_3N)_4Co\begin{matrix}NH_2\\OH\end{matrix}Co(NH_3)_4\right](NO_3)_4+HNO_3=\left[\begin{matrix}(H_3N)_4\\O_3N\end{matrix}Co{-}NH_2{-}{-}{-}Co\begin{matrix}(NH_3)_4\\OH_2\end{matrix}\right](NO_3)_4$$

Nitratoaquooctammine-μ-amido dicobalt(III) salts

All of these series are aquo-series and consequently act acidic, just as the aquo-salts of the mononuclear cobalt ammines do.[1] Of the five anions only four are ionically bonded, so that the

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[1]Ber. d. d. Chem. Ges. (1907) 40:4102

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general formula for the salt formed by double displacement should be written as

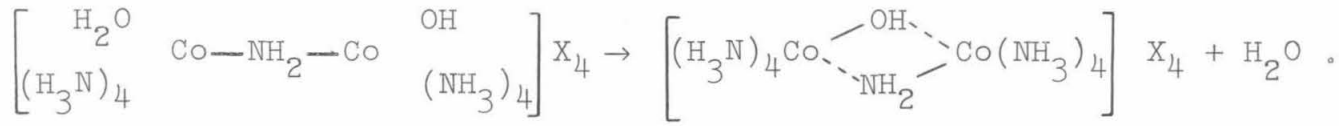
$$\left[\begin{matrix}X\\(H_3N)_4\end{matrix}Co{-}NH_2{-}{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right]Y_4\ .$$

In aqueous solution, hydration, i.e., the formation of aquo salts, occurs exactly as in the chloro, bromo and nitrato salts of the simple cobalt ammines:

$$\left[\begin{matrix}X\\(H_3N)_4\end{matrix}Co{-}NH_2{-}{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right]Y_4+H_2O=\left[\begin{matrix}H_2O\\(H_3N)_4\end{matrix}Co{-}NH_2{-}{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right]XY_4.$$

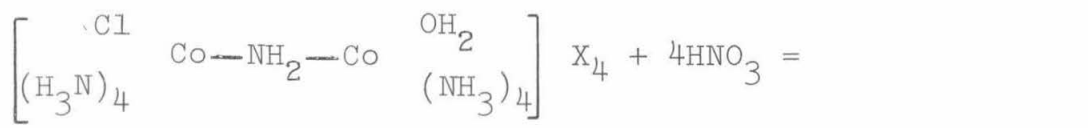
These diaquo salts, which are naturally more extensively hydrolyzed than the monoaquo salts, can spontaneously revert to the octammine-μ-amido-μ-hydroxo dicobalt(III) salts. [13]

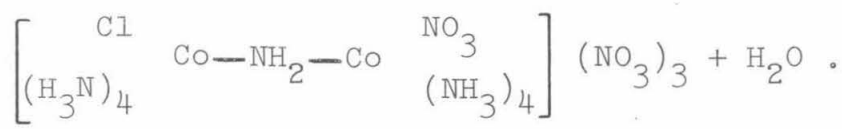
$$\left[\begin{matrix}H_2O\\(H_3N)_4\end{matrix}Co{-}NH_2{-}{-}Co\begin{matrix}OH_2\\(NH_3)_4\end{matrix}\right]X_5\rightarrow\left[\begin{matrix}H_2O\\(H_3N)_4\end{matrix}Co{-}NH_2{-}Co\begin{matrix}OH\\(NH_3)_4\end{matrix}\right]X_4+HX$$



This is verified by the fact that after some time octammine-μ-amido-μ-hydroxo salts, which are only slightly soluble, do crystallize out of solutions of the acido-aquo salts.

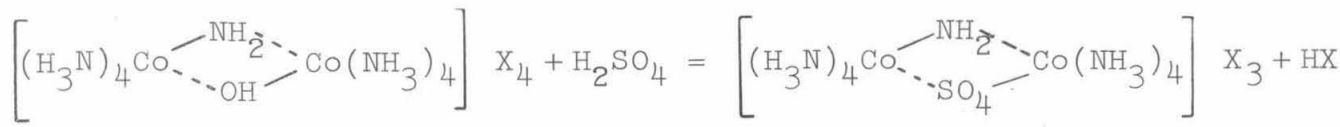
The acidoaquo salts can under certain conditions be converted into diacido salts. For example, this is the case with the chloroaquo series, which yields a water-free salt when treated with concentrated nitric acid:



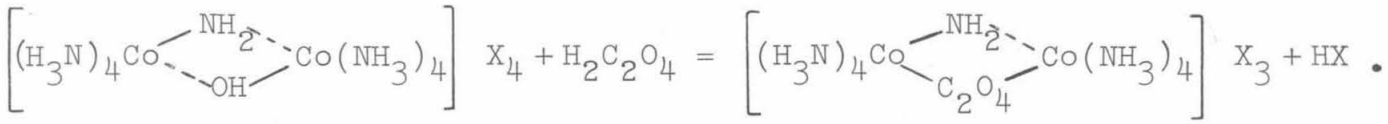


Chloronitratooctammine-μ-amido-dicobalt(III) salts

The preparation of diacido salt compounds is particularly simple if divalent acids such as sulfuric acid or oxalic acid are used. Sulfato series and oxalato series are obtained whose structures can be formulated in the following way:



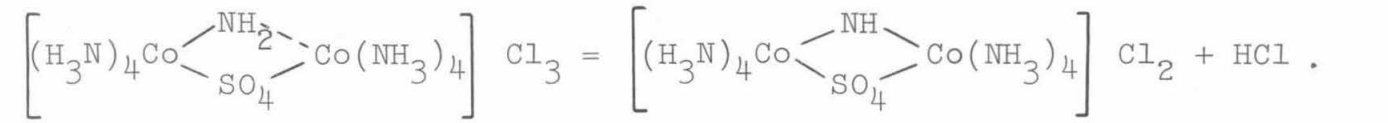
Octammine-μ-amido-μ-sulfato dicobalt(III) salts



Octammine-μ-amido-μ-oxalato dicobalt(III) salts

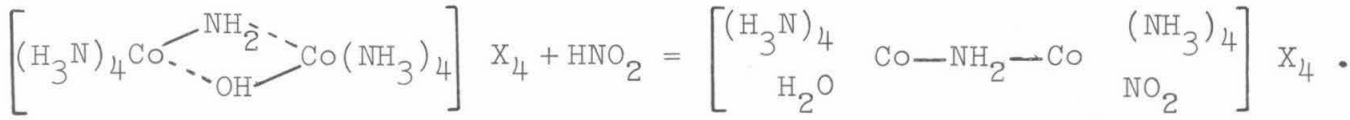
Since the divalent anion is bonded to both cobalt atoms in these compounds, a very stable complex is formed. This can be ascertained from the fact that in pure aqueous solution these compounds will ionize only very slowly or not at all. The salts of the sulfato and oxalato series are accordingly completely [14] stable in aqueous solution.

The chloride of the sulfato series has an interesting behavior; on being heated, it loses hydrogen chloride and thus changes into octammine-μ-imido-μ-sulfato dicobalt chloride:†

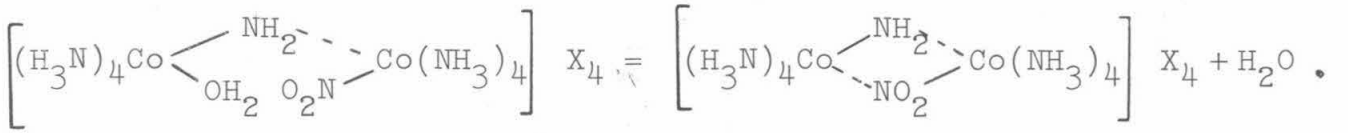


The nitrate of this series can also be produced, namely, by triturating octammine-μ-amido-μ-sulfato dicobalt(III) nitrate with ammonia.

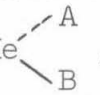
Nitrous acid exhibits a different character from that of the other monobasic acids in relation to the mechanism of its reaction with the octammine-μ-amido-μ-hydroxo dicobalt salts. It, too, reacts with these salts by rupturing the bridging bond and forming a nitrito series, initially probably in the sense of the following equation:

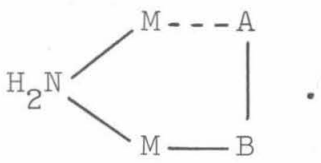


However, the nitrite group in the coordination sphere of the one cobalt atom immediately displaces the water molecule bonded to the second cobalt atom by forming a coordinative bond to that cobalt atom:

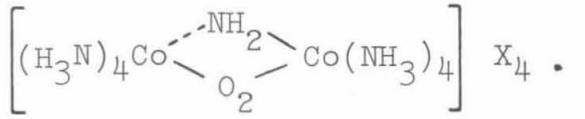


It is apparent from the following facts that the resulting nitrito compound has the latter formula above: 1) The salts of the nitrito series can be obtained water-free; 2) The salts are neutral in solution, in contrast to the behavior of the acidoaquo salts formed with hydrochloric acid, hydrobromic acid, etc.; 3) The nitrito group in the salts of the new series is extraordinarily tightly bound. On the one hand the bond between [15] a nitro group and a cobalt atom (for example, in the nitro-pentammine cobalt salts, the dinitrotetrammine cobalt salts, etc.) can be broken by heating the compound with hydrochloric acid or hydrobromic acid or other such mineral acids, with replacement of the nitro group by other acid residues. On the other hand, this cannot be successfully carried out with the salts of the nitrito series; they are completely stable even when boiled in concentrated hydrochloric acid. The hypothesis that this nitrito group is a bridging group between the two cobalt atoms in such salts explains their remarkable stability and other unusual properties most satisfactorily.

It must be emphasized that this nitrito series, because of its singular constitution, is a new type of inner complex salt. While in the usual inner complex salts the acid residue is bonded to the same metal atom by one primary and one secondary valence bond,  , the situation in the present case is such that the primary and secondary valences are successfully satisfied by two metal atoms joined together by another group (here NH_2):



D. Octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts



In addition to the red octammine-μ-amido-μ-hydroxo dicobalt(III) sulfate, Vortmann's sulfate contains a green sulfate that upon treatment with nitric acid transforms to a green nitrate. This can be isolated easily, and from it other salts of this new series can be easily obtained. The elucidation of the constitution of this series of salts encountered great difficulties, but it is now complete. [16]

The new green series is closely related to the octammine-μ-amido-μ-hydroxo dicobalt(III) salts. This comes about, firstly, because of the close similarity of their composition where, as far as is analytically demonstrable, the new series differs from

that of the octammine-μ-amido-μ-hydroxo dicobalt(III) salts only in that it contains one extra oxygen atom, and secondly from the fact that the salts of the green series can be converted into octammine-μ-amido-μ-hydroxo dicobalt(III) salts by reduction. The simplest way of carrying out the reduction is to treat a solution of the green salt and acetic acid with potassium iodide or sodium iodide. The reaction proceeds with the liberation of iodine and a periodide. Sodium thiosulfate solution is then added until the solution takes on a clear red color. The red salt thus formed is then triturated with ammonium bromide to give octammine-μ-amido-μ-hydroxo dicobalt bromide. The reduction may also be carried out with potassium thiocyanate; this is fully described in the experimental section.

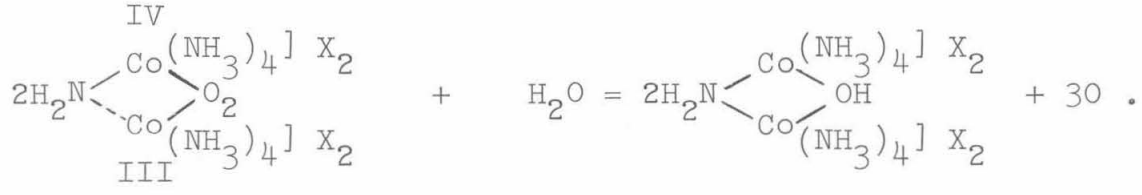
The octammine-μ-sulfato dicobalt salts are generated by reduction with sulfurous acid; this is not surprising in view of the easy formation of this series of compounds from sulfuric acid and octammine-μ-amido-μ-hydroxo dicobalt(III) salts. Nitrous acid also acts as a reducing agent and produces octammine-μ-amido-μ-nitrito dicobalt(III) salts.

From the behavior we have just described, it must be concluded that in the green salts there is a higher oxidation state of the complex radical of the octammine-μ-amido salts. The nature of this higher oxidation state could be established in the following way. It has been found when the sulfate of the green series is heated with concentrated sulfuric acid, first of all oxygen is liberated, whereupon it dissolves to give a violet solution. If the mixture is heated more strongly,

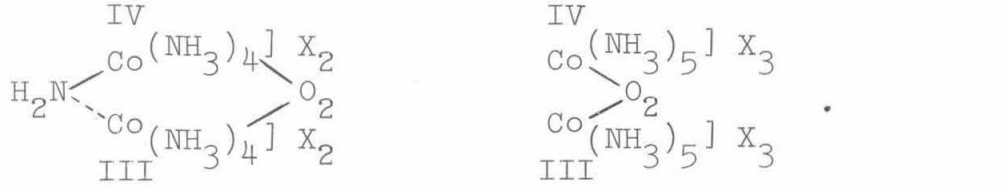
nitrogen is evolved and the cobalt precipitates as the rose-colored cobalt(II) sulfate. The amount of nitrogen evolved per molecule [17] of the sulfate corresponds exactly to the conversion of two trivalent cobalt atoms to two divalent ones, i.e., for every two cobalt atoms the amount of nitrogen evolved corresponds to 2/3 atom. It can be concluded from this that in the first phase of the reaction all of the cobalt is converted to the trivalent state, and in the second phase of the reaction all the cobalt is changed from trivalent to divalent. This conclusion was verified through control experiments with octammine-μ-amido-μ-hydroxo dicobalt(III) sulfate and with simple cobalt-ammines. Such experiments have shown that in all cases an amount of nitrogen corresponding to 2/3 atom evolves from octammine-μ-amido-μ-hydroxo dicobalt(III) sulfate, and that all sulfates of the simple cobalt(III) ammines are transformed into cobalt sulfate when heated with sulfuric acid, releasing an amount of nitrogen equivalent to the conversion of the cobalt from trivalent to divalent.

The amount of oxygen formed from the green sulfate in the first phase amounts to 1 1/2 atoms of oxygen for every two cobalt atoms. This great amount of oxygen, if all of it serves to raise the oxidation state of the two cobalt atoms, would require that in the green sulfate one cobalt be tetravalent and one pentavalent. Such an assumption is most improbable. A much better assumption would be that the oxygen is present as peroxide. If one assumes this, and considers that in every case one of the cobalt atoms is more than trivalent--because a reduction must occur for the octammine-μ-amido-μ-hydroxo dicobalt(III) salts to be formed--then

the green sulfate must contain one tetravalent and one trivalent cobalt atom, as is indicated in the following formulation of the transformation into the μ-amido-μ-hydroxo series:



This interpretation has found substantial support in the close analogy between the salts of this green series and the similarly green salts of the anhydrooxycobalt-ammines (which A. Mylius and I have thoroughly investigated) and which likewise possess one tetravalent and one trivalent cobalt atom. This is immediately obvious from a comparison of their respective formulas: [18]

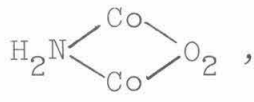


New green series

Anhydrooxycobalt-ammines

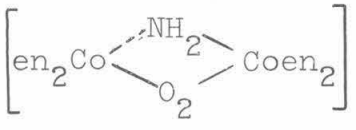
Our complex green series is thus none other than the anhydrooxycobalt ammine series of the μ-amido dicobalt(III) salts. In addition, this description best fits the total behavior of these salts.

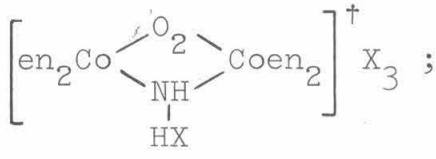
The central framework,

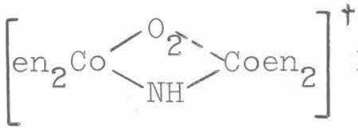


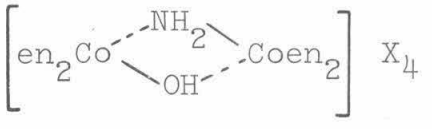
of the complex radical of this series is remarkably stable. It is possible to replace all of the ammonia molecules with ethylenediamine by warming the salts of the just described series with 10% aqueous ethylenediamine. Salts of the tetraethylenediamine-μ-amido-μ-peroxo series can be prepared in this way.

E. Tetraethylenediamine-μ-amido dicobalt(III) salts, tetraethylenediamine-μ-ammonium dicobalt(III) salts, tetraethylenediamine-μ-imido-μ-peroxo dicobalt(III,IV) salts, and tetraethylenediamine-μ-amido-μ-hydroxo dicobalt(III) salts





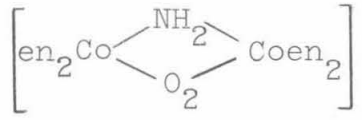




The reaction path leading to the preparation of the first of these compounds has just been discussed.

During the attempts to isolate the new series of compounds from the reaction mixture of octammine-μ-amido-μ-peroxo dicobalt (III,IV) nitrate in 10% aqueous ethylenediamine, it was observed that different salts were obtained depending on whether or not the reaction mixture was neutralized with nitric acid while very [19]

cold or at room temperature. If neutralization is carried out at very low temperatures, a red nitrate precipitates; if at room temperature, a green nitrate precipitates. These salts differ in composition only in that the red salt contains two molecules of water, while the green salt is water-free; they correspond to the following formulas:

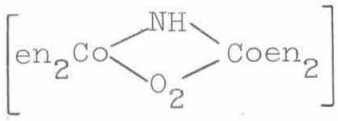


Red salt Green salt

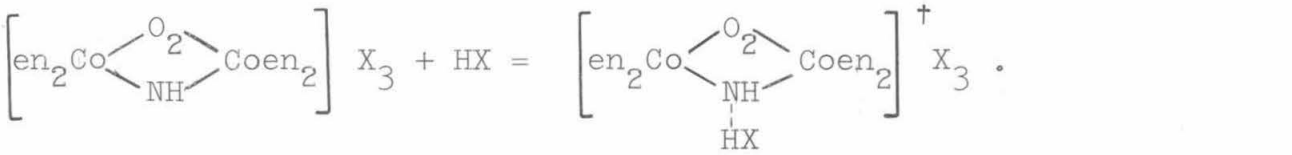
If the red salt is heated in aqueous nitric acid solution, the red color soon changes to green and the red salt is thus transformed into the green one. Other red salts, for example, the bromide, can be prepared from the red nitrate; similarly, green salts can be made from the green nitrate. A substantial difference between the red and green salts is that the red ones are strongly acid in aqueous solution while the green salts give a completely neutral reaction.

Information as to the basis for the isomerism of the two series was obtained in the following way.

Both the green as well as the red salts lose one molecule of acid on reaction with ammonia, and thus become tetraethylenediamine-μ-imido-μ-peroxo dicobalt(III,IV) salts:



The iodide of this series is easily isolated as it is only slightly soluble. If an aqueous solution of the iodide is shaken with silver chloride, a solution of the corresponding chloride results. If this solution, which has a brown color, is carefully neutralized with HCl until the color changes to red, and is then treated with solid ammonium bromide, the red bromide will precipitate out. If this red bromide is heated with water containing hydrobromic acid, it converts to the green bromide. It thus follows that the imido dicobalt series can be first converted to the red salts by the addition of acid, and these may then be easily changed into the green salts by heating with dilute acid. Using formulas for these processes we get the following picture: [20]

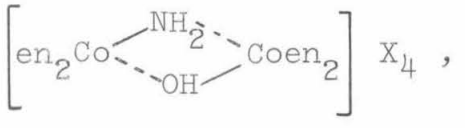


In the first phase of this reaction the acid molecule attaches to the amido group. This agrees well with the red salts being partially hydrolyzed in aqueous solution and thus being acidic.

The red salts are unstable, however, and transform into the green salts corresponding in constitution to the octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts. According to our earlier deductions, these green salts can have only the following formula:

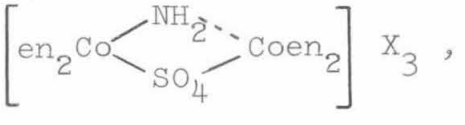
The isomerization consequently arises from the transformability of the secondary valence bond of the amido hydrogen into a primary valence bond, while the primary valence bond between the bridging nitrogen and one of the cobalt atoms is transformed into a secondary valence bond. In this way, the fourth anion becomes indirectly bonded to the cobalt, and becomes equivalent to those as in the normal cobalt-ammine salts; this explains the origin of the neutral reaction in solution. We have thus associated the isomerism of the red and green salts with valence isomerism. To differentiate between the isomeric salts, I have named the red ones tetraethylenediamine-μ-ammonium-μ-peroxo dicobalt(III,IV) salts, and the green ones, tetraethylenediamine-μ-amido-μ-peroxo dicobalt(III,IV) salts. [21]

Both the red and the green salts can be reduced by treating their solutions with acetic acid and potassium iodide. Tetraethylenediamine-μ-amido-hydroxo dicobalt(III) salts,



are thus formed.

The research on these salts has not yet been completed. Their behavior corresponds completely to that of the octammine-μ-amido-μ-hydroxo dicobalt(III) salts. For example, this is already evident since they can be converted to the sulfato series,



with the greatest of ease.

F. Octammine-di-μ-hydroxo dicobalt(III) salts and tetra-ethylenediamine-di-μ-hydroxo dicobalt(III) salts

$$\left[(H_3N)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]X_4 \text{ and } \left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right]X_4 .$$

These two series of compounds have been synthesized from the following two series of hydroxoaquo compounds:

$$\left[\begin{matrix}HO\\H_2O\end{matrix}Co(NH_3)_4\right]X_2 \quad \text{and} \quad \left[\begin{matrix}HO\\H_2O\end{matrix}Coen_2\right]X_2 .$$

The sulfate of the first and the dithionate of the second series of compounds lose water after being heated for a long period, whereupon the following reactions take place:

$$2\left[(H_3N)_4Co\begin{matrix}OH\\OH_2\end{matrix}\right]SO_4 = 2H_2O + \left[(H_3N)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right](SO_4)_2 \qquad [22]$$

$$2\left[en_2Co\begin{matrix}OH\\OH_2\end{matrix}\right]S_2O_6 = 2H_2O + \left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right](S_2O_6)_2 .$$

A large variety of other salts can be prepared in a pure state by triturating the sulfate or dithionate, which are almost insoluble in water, with ammonium salts.

The salts of the ammines are a dark ruby red, those of the ethylenediamine series being more violet-red in color. Several of the former have already been described[1]; others will be

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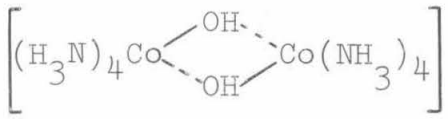
[1] Ber. d. deutsch. Chem. Ges. (1907) 40:4434

characterized in the experimental part of this paper. The ethylenediamine salts, until now unknown, will be described in the experimental section.

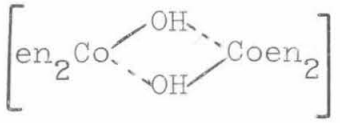
It is characteristic of the salts of both of these series that they form neutral aqueous solutions, and do not give aquo salts with dilute mineral acids. From this it is evident that the hydroxy groups are masked, i.e., they are involved in co-ordinative bonding. This cannot be expressed in such a clear way by any structural formula except that established for the new series.

A second important characteristic of these compounds is their decomposition in concentrated hydrochloric acid, which proceeds in the following manner:



$$Cl_4 + 2HCl = [(H_3N)_4Co(OH_2)_2]Cl_3 + [Cl_2Co(NH_3)_4]Cl$$

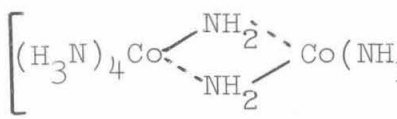
and



$$Cl_4 + 2HCl = [en_2Co(OH_2)_2]Cl_3 + [Cl_2Coen_2]Cl \ .$$

The fact that cis-diaquo and the cis-dichloro salts (Violeo salts) are formed is of great importance in the determination of the configuration of the spatial isomers of cobalt ammines.

G. Octammine-di-μ-amido dicobalt(III) salts [23]



$$X_4 \ .$$

This series of compounds is the only one of the polynuclear cobalt ammine series for which a reliable preparation scheme cannot be given. Their formation has been observed on occasion in the preparation of 1,2 dichlorotetrammine cobalt(III) chloride from the previously discussed octammine-di-μ-hydroxo dicobalt(III) salts. If the crude Violeo chloride is dried in a desiccator over phosphorous pentoxide, the surface sometimes takes on a reddish color. In spite of numerous attempts, more definite conditions under which this modification can occur could not be found. If the partially reacted salt is dissolved in water and the solution treated with sodium dithionate after being allowed to stand for about one-half hour, an insoluble red-brown dithionate precipitates out. This is converted to an ochre red bromide by triturating it with ammonium bromide. The analysis of this compound shows that it has the formula

$$\left[(H_3N)_4Co\begin{matrix}NH_2\\NH_2\end{matrix}Co(NH_3)_4\right]Br_4 \cdot H_2O \ .$$

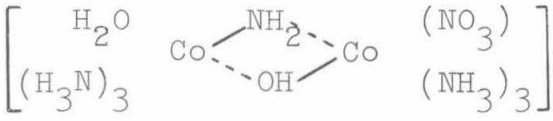
H. <u>The hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series and its derivatives</u>

The starting material for the preparation of the salts of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series, which correspond to the formula :

$$\left[(H_3N)_3Co\begin{matrix}NH_2\\OH\\OH\end{matrix}Co(NH_3)_3\right]X_3$$

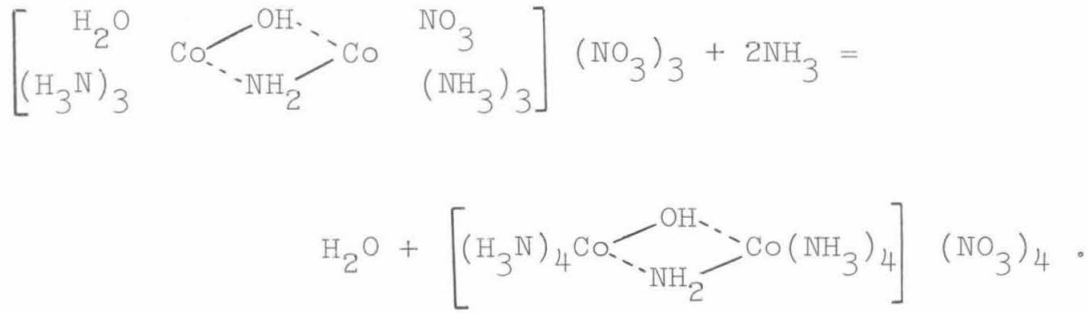
is the crude product designated as Melano chloride, which is obtained by adding hydrochloric acid to an air-oxidized solution of cobalt(II) chloride. By an exchange reaction with silver nitrate in nitric acid solution a slightly soluble red nitrate [24] is obtained which yields the bromide of the desired series on treatment with ammonium bromide. All of these salts are brown-red in color.

To prove the presence of the μ-amido bridge, the red nitrate is converted into a new nitrate by reaction with nitric acid. This salt,



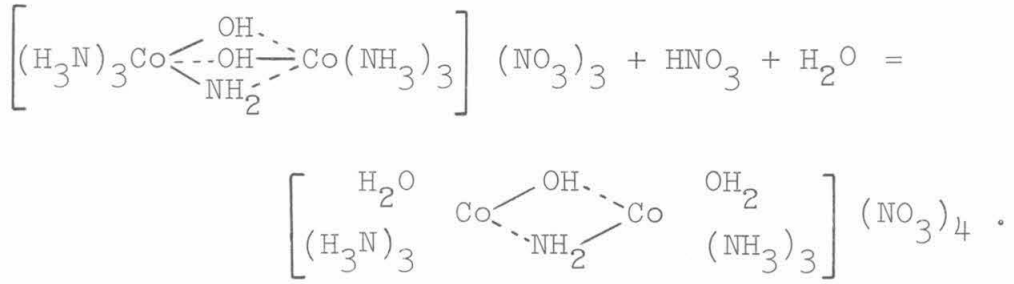
is recognized to be nitroaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate.

In liquid ammonia this nitrato nitrate takes up two molecules of ammonia and becomes octammine-μ-amido-μ-hydroxo dicobalt(III) nitrate:

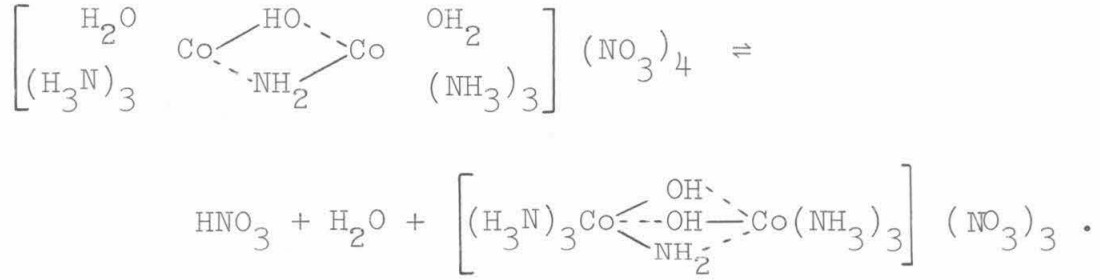


Since this latter series can be transformed, as has been shown, into decammine-μ-amido dicobalt salts, the hexammine series must also contain a μ-amido bridge.

One of the hydroxo bridges of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series can be split more easily than the second, thereby forming diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) salts. One such cleavage occurs, for example, when the nitrate of the μ-amido-di-μ-hydroxo series is recrystallized from nitric acid solution. The following reaction takes place:

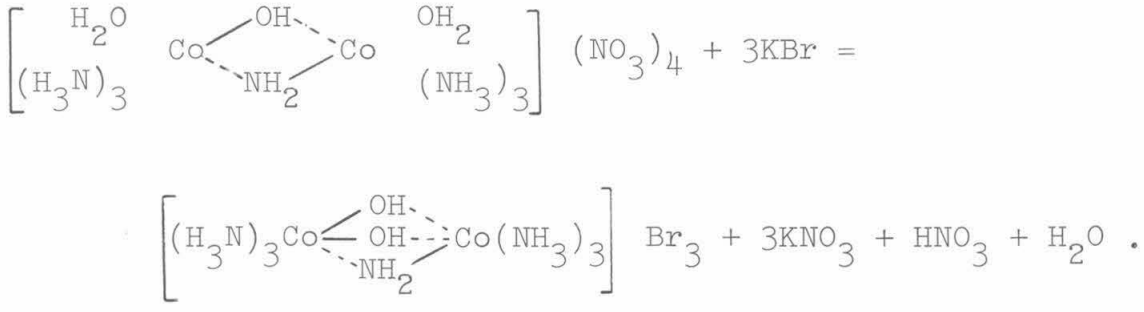


The possibility of isolating this salt depends in any case on its low solubility, because of which it is precipitated from solution by nitric acid according to the equilibrium described by the following equation: [25]

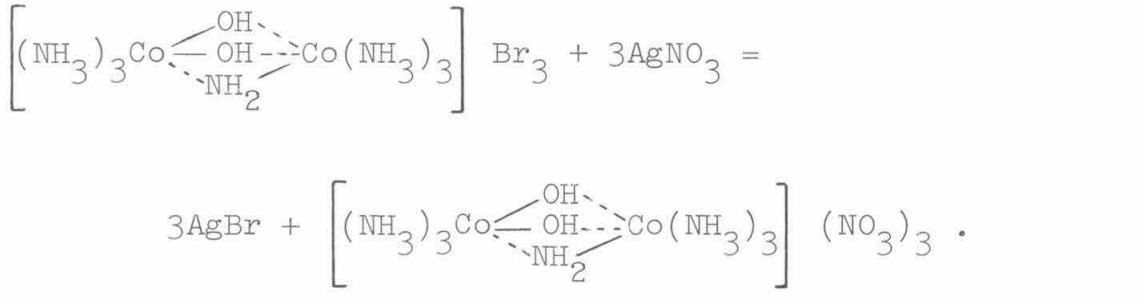


In fact, it can be verified that the same solution yields the strongly acidic diaquo nitrate with ammonium nitrate. On the other hand, the bromine or iodine salts of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series are obtained with ammonium

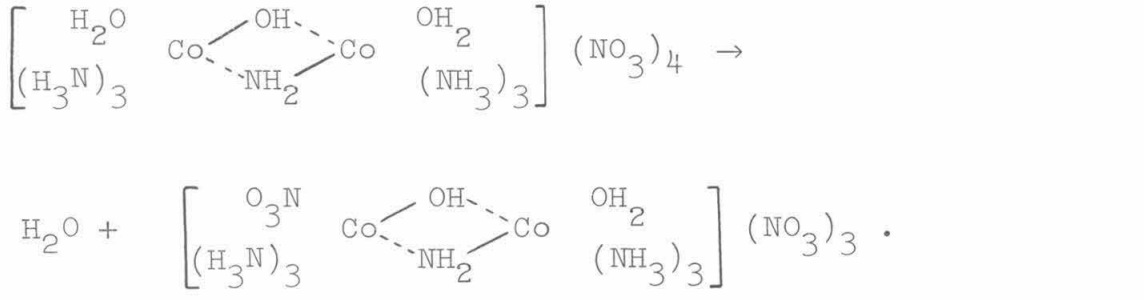
bromide or potassium iodide, respectively. For example:



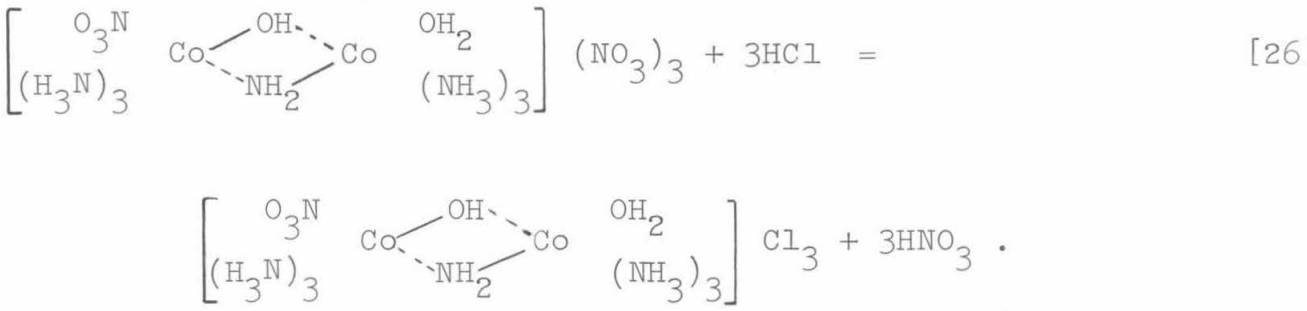
The bromide or the corresponding iodide thus formed can be converted to the nitrate of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series by reaction with silver nitrate:



If the solution of the diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate is heated with concentrated nitric acid, the brown-red nitratoaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate mentioned above is produced:

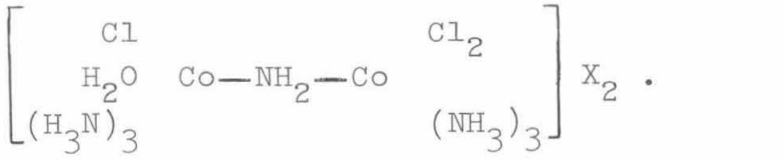


That only three nitrate groups are ionically bonded in this salt can be proven by their replacement as, for example, in the following reaction with hydrochloric acid:



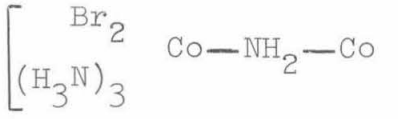
[26]

Various sulfato and oxalato series, which have not yet been thoroughly investigated, are formed from the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts on reaction with sulfuric acid and oxalic acid respectively. If solutions of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts are heated with hydrochloric acid, an extraordinarily insoluble black-violet salt separates out in the form of small crystals. This is the pure Melanochloride. Our investigation has shown that it contains two ionically bonded chlorine atoms; hence, the salts of the Melano series must be designated as trichloroaquo-hexammine-μ-amido-dicobalt(III) salts and correspond to the following constitutional formula:



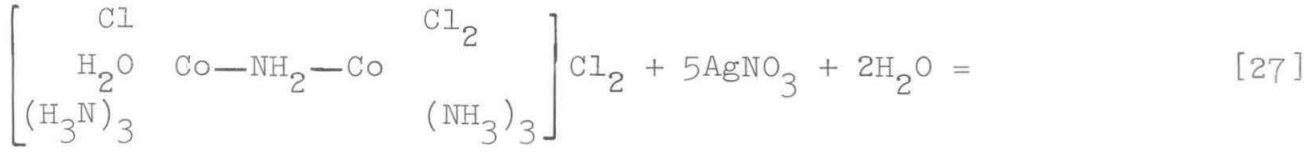
If the Melanochloride is heated at 60-70°, it loses the water and transforms to tetrachlorohexammine-μ-amido dicobalt(III) chloride with essentially no change in external appearance.

Hydrobromic acid converts the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts into tetrabromohexammine-μ-amido dicobalt(III) bromide:



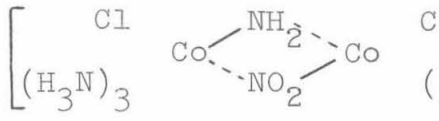
The salts of this latter series have a green-black color and are similarly very insoluble in water.

The salts of the trichloro, tetrachloro and tetrabromo series can be changed back into tetraquohexammine-μ-amido dicobalt(III) nitrate by digestion in silver nitrate solution that has been weakly acidified with nitric acid.



[27]

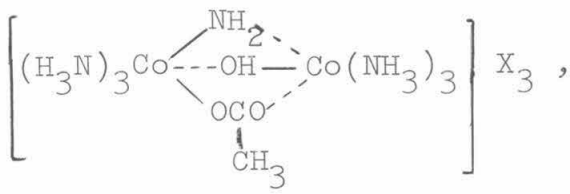
Treatment of a solution of the diaquo nitrate with nitrous acid gives a deep orange-gold solution from which a brownish, flesh-colored chloride can be precipitated by adding hydrochloric acid and heating. This compound is dichlorohexammine-μ-amido-μ-nitrito dicobalt(III) chloride, which has the following formula:



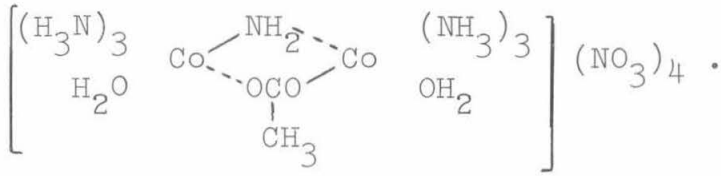
The nitrito group in this compound is at least as tightly bonded as in the octammine-μ-amido-μ-nitrito dicobalt salts; it cannot be removed from the complex radical without completely destroying the compound. Of the four chlorine atoms, two are not ionically bonded.

Diaquohexammine-μ-amido dicobalt(III) nitrate exhibits a very peculiar behavior in acetic acid which was disturbing to our investigations for some time.

Acetic acid is often added to solutions of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate in order to protect against decomposition during heating. This is a common procedure with the simple cobalt ammines. However, the analytical data obtained for salts isolated from such solutions often could not be reconciled with that calculated for the expected compounds. Furthermore, the salts concerned behaved anomalously in the sense that they no longer underwent the typical melano reaction (precipitation of a black salt upon heating with hydrochloric acid). It was finally discovered that the reason for this peculiar behavior was that the acetate group can serve as a complexing agent in the polynuclear cobalt ammine radical. The compounds thus formed, hexammine-μ-amido-μ-hydroxo-μ-acetato dicobalt(III) salts, [28]



are extremely stable and the acetate contained in them is especially tightly bound. The acetate group is not lost by either boiling in water or by recrystallization. The salts of the μ-acetato series are bright red and possess numerous analogs with the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts. For example, the salt obtained by precipitation from nitric acid solution is not the nitrate of the μ-acetato-μ-hydroxo series, but the nitrate of the diaquo hexammine-μ-amido-μ-acetato series:



As in the di-μ-hydroxo salts, one of the hydroxo bridges is easily cleaved by nitric acid.

The ability of the acetate anion to serve as a bridging group between the two cobalt atoms and the great stability of these bonds is of theoretical interest because they furnish us with an important reference point for the discussion of the molecular structure of complex chromium acetates and analogous compounds, which similarly contain very stably bonded and difficult to detect acetate and higher organic acid residues. I have convinced myself that not only acetic acid, but other organic acids too can form such bridges. This topic will be discussed further in a later paper.

I. Hexammine-μ-amido-μ-hydroxo-μ-peroxo dicobalt(III,IV) salts

In addition to the salt which gives diaquohexammine-μ-amido-di-μ-hydroxo dicobalt(III) nitrate on addition of silver nitrate, the crude Melano chloride contains a second salt which yields large flaky crystals of a green nitrate on addition of silver nitrate. On treatment with hydrochloric acid, a very difficultly soluble gray-black chloride forms from this, which is easily confused with the ordinary Melano chloride because of its similar appearance, but which differs from it in composition by possessing one less chlorine atom and two more oxygen atoms. The following in particular must be taken into consideration in the determination of the constitution of this new green polynuclear series. [29]

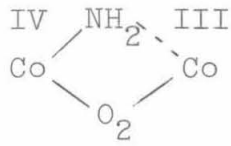
1. The new series yields the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series on being reduced with potassium iodide and acetic acid. It follows from this that the bonding of the cobalt atoms and the ammonia molecules in this green series is the same as that in the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) series. Its complex radical must consequently contain the following nucleus: $(H_3N)_3Co{-}NH_2{-}Co(NH_3)_3$.

2. This new series is also obtained in the decomposition of the octammine-μ-amido-μ-peroxo dicobalt(III,IV) series. This may be accomplished by heating an aqueous solution of an octammine-μ-amido-μ-peroxo dicobalt(III,IV) salt and ammonium chloride. The nearly insoluble chloride is precipitated by saturating the reaction mixture with hydrochloric acid. This chloride differs from the chloride of the μ-amido-μ-peroxo series

only in that it contains two less ammonia molecules in the cation. The conversion can be expressed by the equation:

$$H_2NCo_2(NH_3)_3O_2Cl_4 = 2NH_3 + H_2NCo_2(NH_3)_6O_2Cl_4 \ .$$

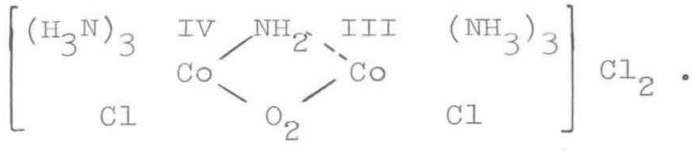
On the basis of this formation reaction and considering the similarity of the colors of the salts of the two series (both are green), it may be concluded that the new series contains the same very stable molecular nucleus



as the octammine-μ-amido-μ-peroxo series.

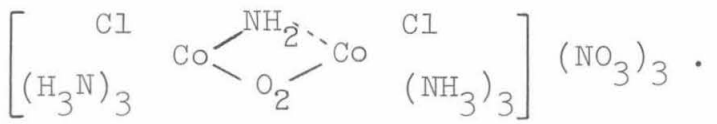
This conclusion could also be verified by the observation [30] that the octammine-μ-amido-μ-peroxo salt can be recovered from the above mentioned black chloride by treatment with liquid ammonia.

Combining these two important conclusions, we can arrive at the formula of the chloride by adding six ammonia molecules and four chlorine atoms to the above molecular nucleus. This leads us to the following constitutional formula:

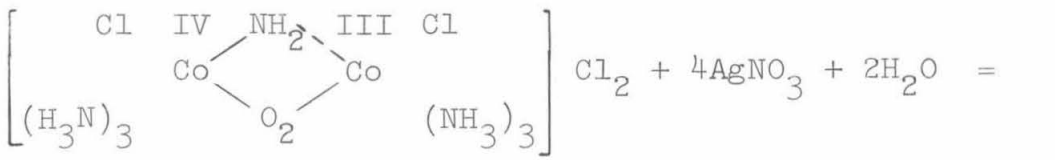


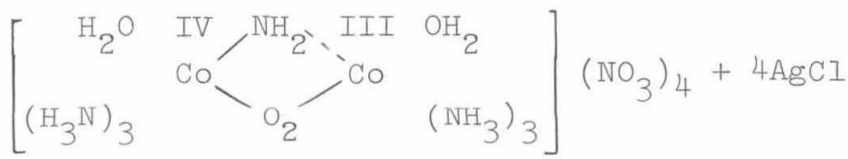
According to this, the chloride contains only two ionically bonded chlorine atoms. This is experimentally verifiable, as

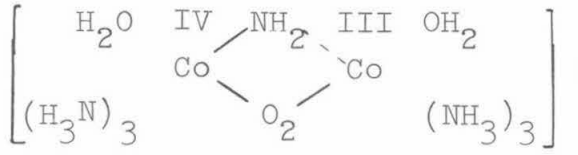
only two chlorine atoms were replaced by nitrate groups on treatment with nitric acid, forming the nitrate with the following formula:



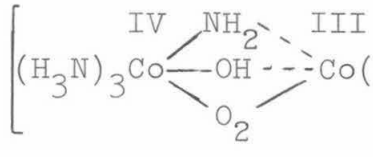
This salt is designated as <u>dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate</u>. This constitutional formula is the one most consistent with the other transformation reactions of the chloride. The exchange reaction between the chloride and silver nitrate yields a green nitrate containing only three nitrate groups instead of four. This can be explained by the existence of a diaquo nitrate intermediate which releases nitric acid and water to form hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) nitrate:





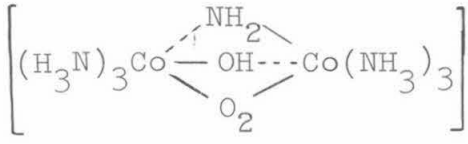


$(NO_3)_4$ = [31]

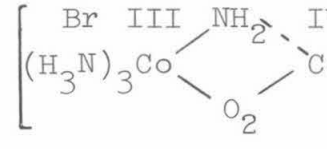


$(NO_3)_3 + HNO_3 + H_2O$.

This process corresponds completely to the proven transformation of diaquo octammine-μ-amido dicobalt(III) salts into octammine-μ-amido-μ-hydroxo dicobalt(III) salts as well as of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate into hexammine-μ-amido-μ-hydroxo dicobalt(III) bromide. The salts corresponding to the green nitrate obtained from these by double substitution are consequently hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) salts which thus represent the anhydro oxycobalt ammine series of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts. It is thus understandable that the salts of this series give hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts when reduced. The cleavage of the hydroxo bridge by hydrochloric acid or hydrobromic acid corresponds to the reaction observed in other series possessing hydroxo bridges. The reaction with hydrobromic acid, which we have investigated, leads to the formation of dibromo hexammine-μ-amido-μ-peroxo dicobalt(III,IV) bromide.

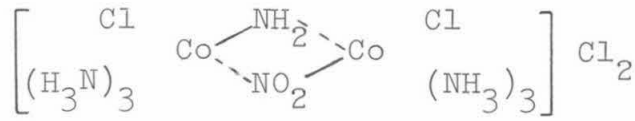


$X_3 + 4HBr =$



Br_2 .

Hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) nitrate is also reduced by nitrous acid, with simultaneous entry of a nitrato group into the molecule. By heating the resulting yellow-brown reaction mixture with hydrochloric acid, dichloro-hexammine-μ-amido-μ-nitrito dicobalt(III) chloride,



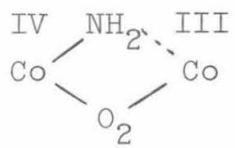
which has already been mentioned above, precipitates out.

The nitrito group in this compound, owing to its central location, exhibits the characteristic, particularly strong bonding.

J. On an isomer of dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) chloride and an isomer of dibromo-hexammine-μ-amido-μ-peroxo dicobalt(III,IV) bromide [32]

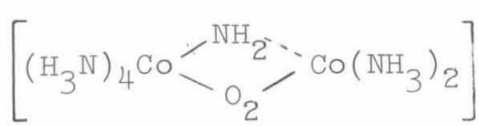
If solutions of octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate are heated with an excess of ammonium carbonate rather than with ammonium chloride and are then treated with concentrated hydrochloric or hydrobromic acid, a dark green chloride or bromide is obtained which is isomeric with the salts discussed in the previous section. The composition of the new salt is the same as that of its isomer, but its properties are completely different. The new salts are very soluble in water, the solutions having a deep greenish-brown color. They can be reprecipitated from the cold, saturated solutions by the addition of concentrated

hydrochloric or hydrobromic acid. That these salts may be converted back into octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts follow if these salts do contain the characteristic molecular nucleus of the octammine-μ-amido-μ-peroxo salts:

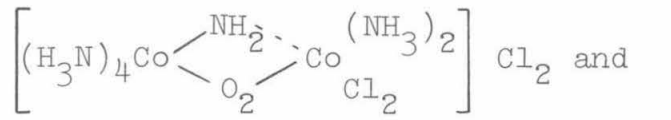


This reconversion is indeed easily effected by simply placing the chloride or bromide in liquid ammonia. The residue left after the evaporation of the ammonia consists nearly quantitatively of octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts.

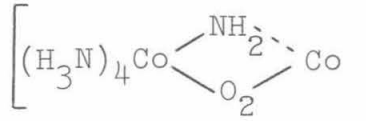
The difference between the new salts and their isomers can only depend on a different arrangement of the ammonia molecules on the two cobalt atoms. This interpretation can be confirmed experimentally by reducing the salts, a process which may be easily carried out, for example, by boiling them in hydrochloric acid. Chloropentammine cobalt chloride and cobaltous chloride [33] are formed as products of the reduction. This finding can only be explained if one cobalt atom in the salt has five nitrogen atoms bonded to it as in the original octammine series. The two ammonia molecules lost by degradation of the salt with ammonium carbonate must have come from the same cobalt atom. For this reason, the new compound must contain the following radical as its nucleus:



One cobalt atom of this radical has two coordination vacancies which are filled by two halogen atoms in the chloride and the bromide. This gives the following constitutional formulas for the two compounds:

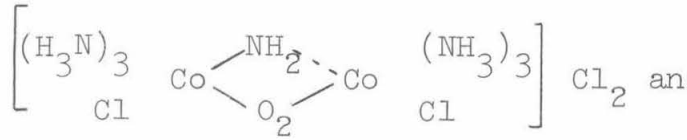


and

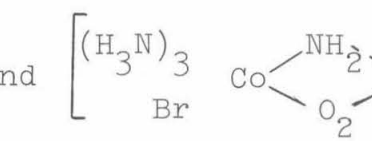


It is not experimentally possible to determine whether the tetravalent or the trivalent cobalt has the fewer ammonia molecules bonded to it.

If the above constitutional formulas are compared with those of their isomers:



and



it is evident that the isomerism depends on the different distribution of the ammonia molecules and the directly bonded halogen atoms on the two cobalt atoms. The salts with an <u>equal distribution of ammonia molecules</u> will be designated as <u>symmetric</u> forms, and those with an <u>unequal distribution</u>, as <u>asymmetric</u> forms, which will be designated in their names by the prefixes <u>sym</u> and <u>asym</u>. The isomerism described here represents a heretofore unobserved kind of isomerism that is similar to organic structural isomerism, as was already discussed in the introduction. For this reason I have designated this type of isomerism as "<u>coordinative structural isomerism</u>." The discovery of this unique isomerism [34]

is another example of how extensively the deductions from co-ordination theory are confirmed by fact.

K. The hexammine-tri-μ-hydroxo dicobalt(III) salts and their derivative series

The hexammine-tri-μ-hydroxo dicobalt(III) salts have been thoroughly described in a prior publication.[1] They correspond

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[1] Ber. d. d. Chem. Ges. (1907) 40:4834

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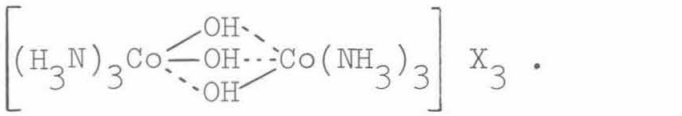
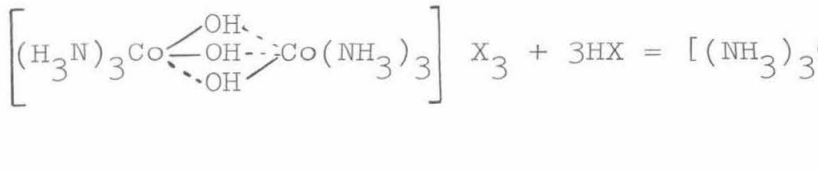
to the following constitutional formula:



The constitution is given unambiguously by the composition of the salts and by the cleavage products resulting from treatment with halogenic acids. The salts are quantitatively broken up into two molecules of triammine cobalt(III) salts in this decomposition, according to the following reaction scheme:



The following salts of the hexammine-tri-μ-hydroxo dicobalt(III) series have been prepared: chloride, bromide, nitrate, sulfate,

dithionate and thiocyanate. A substantial number of series of polynuclear cobalt ammines can be made from the hexammine-tri-μ-hydroxo dicobalt(III) salts; these are discribed in the experimental section. As a rule, these new series are very easily prepared because one of the hydroxyl bridges of the tri-μ-hydroxo salts is extraordinarily easily cleaved by acids. This cleavage occurs, for example, with nitric acid, producing dinitrato hexammine-di-μ-hydroxo dicobalt(III) nitrate:[2]

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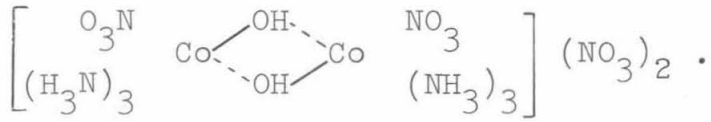
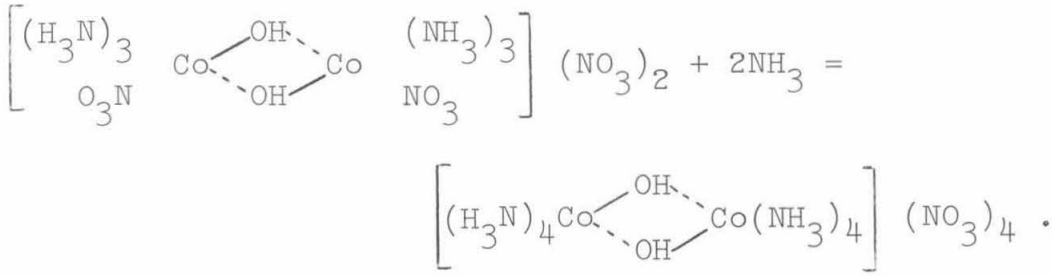
[2]Ber d. d. Chem. Ges. (1908) 41:3879

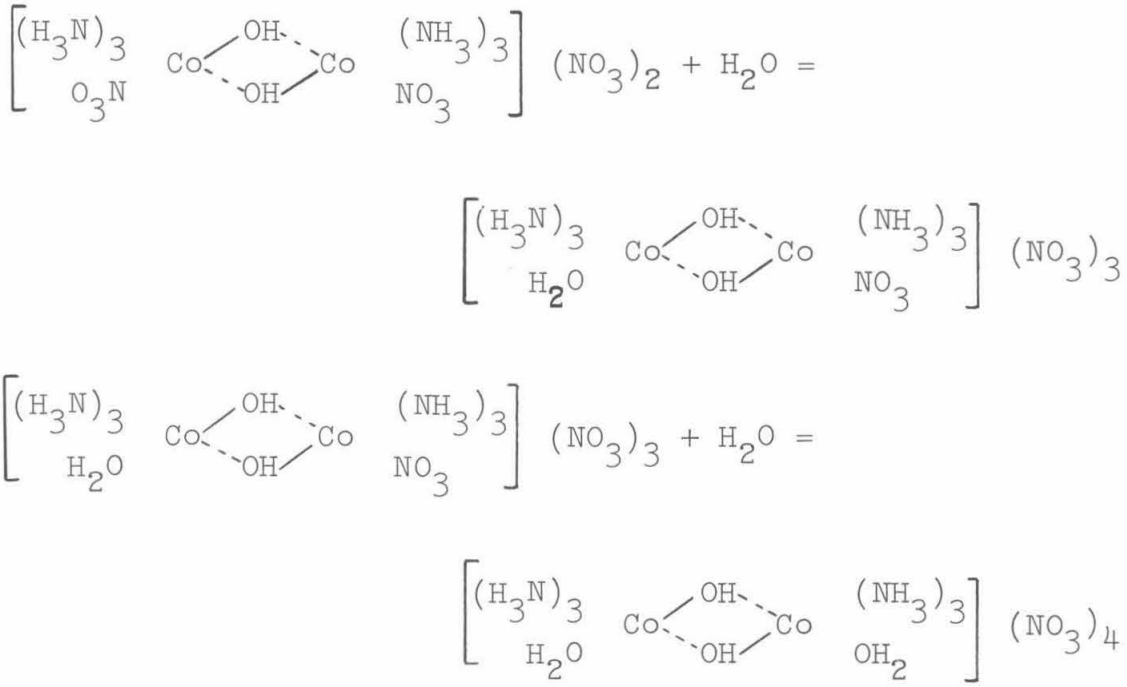


This can then be converted into octammine-di-μ-hydroxo dicobalt(III) nitrate by treatment with liquid ammonia: [35]

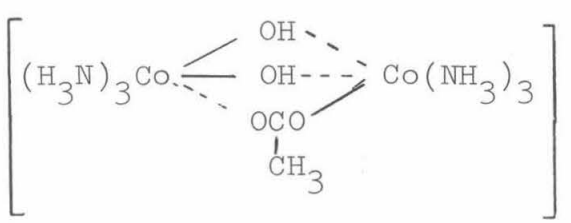


This transformation of the hexammine-tri-μ-hydroxo dicobalt(III) salts into octammine-di-μ-hydroxo dicobalt(III) salts is of considerable value theoretically, for it provides an independent confirmation of the constitutional formulas of the hexammine and octammine-di-μ-hydroxo dicobalt salts, which had been arrived at from considerably different approaches.

In aqueous solution, dinitrato hexammine-di-μ-hydroxo dicobalt(III) nitrate transforms into nitratoaquo and diaquo salts.

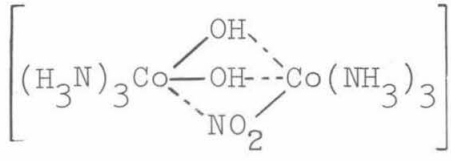


The dithionate series can be isolated from the nitratoaquo series, and the sulfate can be obtained from the diaquo series. Other monovalent acids react in a way similar to nitric acid; for example, acetic acid gives rise to a μ-acetato series. The salts of the latter series are neutral in solution and hence cannot be aquo salts; i.e., the acetate group must form a bridging group as in the hexammine-μ-amido-μ-hydroxo-μ-acetato dicobalt(III) salts. Consequently, we here are dealing with the hexammine-μ-acetato-di-μ-hydroxo dicobalt(III) salts:

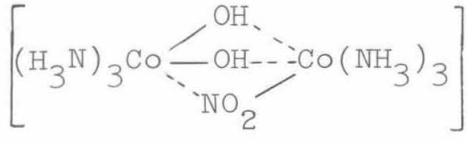


The salts of the acetato series differ from those of the tri-μ-hydroxo series in having a somewhat more blue-red color. The acetate bridge is very stable as is evident since it is not at all dissociated in aqueous solution. The hydroxo bridges are also very stable, as is seen since the salts of the acetato series (for example, the bromide) can be precipitated unchanged [36] from their aqueous solutions by mineral acids.

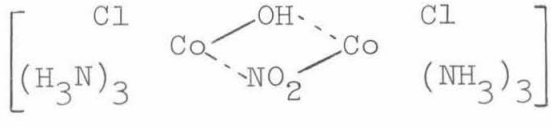
A series of unusually stable compounds results from the reaction of nitric acid with the tri-μ-hydroxo salts. A deep red-yellow hexammine-di-μ-hydroxo-μ-nitrito dicobalt series is first formed in this reaction, and has the formula:



Here, too, the nitrito group shows a remarkably large binding strength. The nitrito bridge is not attacked by hot concentrated hydrochloric or hydrobromic acids, but one of the remaining hydroxo bridges is cleaved whereupon two chlorine or two bromine atoms form direct bonds with the two cobalt atoms. These reactions proceed in the sense of the following equations:

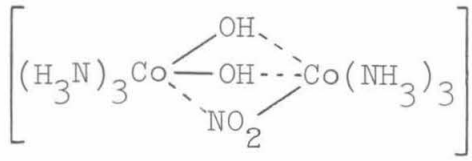


$Cl_3 + HCl =$

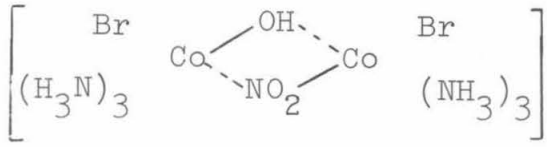


$Cl_2 + H_2O$

and

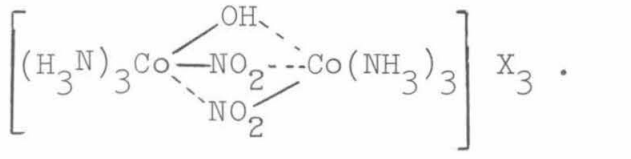


$$\left[(H_3N)_3Co(OH)(OH)(NO_2)Co(NH_3)_3\right]Br_3 + HBr =$$



$$\left[(H_3N)_3Br\,Co(OH)(NO_2)Co\,Br(NH_3)_3\right]Br_2 + H_2O\ .$$

The salts of these two new series are difficultly soluble and have a dark violet color. It has been shown that only two halide groups are ionically bonded in both series. The hexammine-μ-nitrito-di-μ-hydroxo dicobalt(III) series can be regenerated by reaction of the chloro or bromo series with silver nitrate. By treating the chloride of the dichloro series with sodium nitrite in aqueous solution a new series of salts having an orange-red color are obtained. Our investigation has shown that this is the hexammine-di-μ-nitrito-μ-hydroxo dicobalt(III) series, which has the constitutional formula:



$$\left[(H_3N)_3Co(OH)(NO_2)(NO_2)Co(NH_3)_3\right]X_3\ .$$

Both the hydroxyl bridge and the central nitrito groups are [37]
unusually strongly bound. This is evident, for example, from the fact that the chloride of this series can be crystallized out of hot, half-saturated* hydrochloric acid without any structural change.

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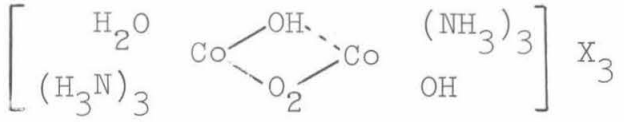
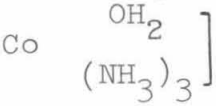
*Translator's note: This probably means a saturated solution diluted to twice its volume.

L. Hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) salts



Great quantities of a brown black nitrate are produced, in addition to the salts of the hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) series, when Melano chloride prepared by cold air-oxidation of ammoniacal cobaltous chloride solution is subsequently treated with silver nitrate. The sulfate of the series corresponding to that of the brown nitrate is well suited for isolation of the series, as it is nearly insoluble. Other salts of the series can be derived from the sulfate by mixing it with the appropriate ammonium salt. The investigation of these salts has shown that they are derived from a polynuclear cobalt ammine radical possessing six nitrogen atoms attached to the two cobalt atoms. It thus could be expected that the new series is related to that of the hexammine-tri-μ-hydroxo dicobalt(III) salts, $[(H_3N)_3Co(OH)_3Co(NH_3)_3]\ X_3$.

In order to clarify this, the known sulfate of this series was cleaved by reacting it with fuming nitric acid and heating it slightly. The nearly quantitative product of this reaction is a blue-red salt that is only slightly soluble in water. The addition of concentrated hydrochloric acid to a warm aqueous solution of the salt gives a rich yield of dichloroaquotriammine cobalt(III) chloride,  Cl. The decomposition

product of the sulfate and fuming nitric acid therefore consists of trinitrato triammine cobalt(III). This implies that the distribution of the ammonia molecules is such that triammine salts can result from cleavage. [38]

The effect of liquid ammonia on the chloride derived from the black sulfate (this procedure will be described later) gives a further insight into the constitution of this series. The primary constituents of the solution of the product of this chloride in hydrochloric acid are hexammine cobalt chloride and chloropentammine cobalt chloride, from which it may be deduced that the two cobalt atoms are not bound together by a μ-amido bridge. It thus follows that each cobalt atom has three ammonia molecules bonded to it. A μ-acetato series, that has been shown to be identical to that derived from the hexammine-tri-μ-hydroxo dicobalt(III) salts, results from the reduction of the brown sulfate by acetic acid and sodium iodide.

It can be concluded from this that the spatial distribution of the ammonia molecules in the brown series is the same as that in the hexammine-tri-μ-hydroxo dicobalt(III) salts. More exact conclusions as to the composition of the molecular nucleus of the brown series have been reached on the basis of the following experimental facts: (1) The complex cation is trivalent since the salts correspond to the general formula RX_3. (2) A mixture of oxygen and nitrogen whose total quantity corresponds to $2\frac{1}{2}$ atoms of oxygen for each pair of cobalt atoms results from the decomposition of the sulfate of this series into cobalt(II) sulfate by heating with concentrated sulfuric acid.

If one considers that the cobalt of the complex cation must be somewhat more than trivalent because a great deal of iodine is released in the reduction of the salt with sodium iodide and acetic acid, then it is very probable that this is a peroxo series with one trivalent and one tetravalent cobalt atom, with properties analogous to those of the other series formed by air oxidation. In fact, the result of the decomposition with concentrated sulfuric acid is consistent with this in that, theoretically, one atom of oxygen can be expected from the peroxo group (O_2), one atom of oxygen can be expected from the [39] conversion of the tetravalent cobalt to divalent, and one-half atom of oxygen from the conversion of the trivalent cobalt to divalent, thus giving a total of $2\frac{1}{2}$ atoms of oxygen per molecule. The complex radical of the brown series, according to the preceding derivation, consequently contains the following atomic combination: $(H_3N)_3Co—O_2—Co(NH_3)_3$. Since this cation is trivalent, two cobalt valences must be satisfied by hydroxyl groups. Only one of these hydroxyl groups can be demonstrated by the formation of salts since only a tetracidic salt, i.e., a salt of a tetravalent complex cation, results from reaction with concentrated hydrochloric acid. The hydroxyl group, for which an acid residue is substituted in the tetracidic salts is in any case present in the form of a hydroxo bridge as it is unaffected by dilute acids.

The second hydroxyl, which must be present as a component of the complex radical, shows no salt-forming property. This

follows from the fact that the salts of the brown series can be dissolved in and reprecipitated from aqueous acid solutions. However, the presence of the hydroxyl group is perceptible in that aqueous solutions of the salts are basic to litmus. Also the fact that the sulfate of the series, which is almost completely insoluble in cold water, immediately goes into solution if a little acetic acid or dilute sulfuric acid is added, shows that the compound still contains one hydroxyl group that is, in a certain sense, reactive.

The peculiarity of the second hydroxyl in not being active in salt formation is plausibly explained if it is being bonded to the tetravalent cobalt atom. In fact, cases have been described in the literature in which tetravalent elements exhibit similar properties. This has, for example, been found to be the case in tetravalent cerium, whose nitrate has the formula $\left[Ce\begin{matrix}OH\\(NH_3)_3\end{matrix}\right] \cdot 4\frac{1}{2}\, H_2O$ and which can be recrystallized from an aqueous nitric acid solution without being converted into cerium tetranitrate.[1] [40]

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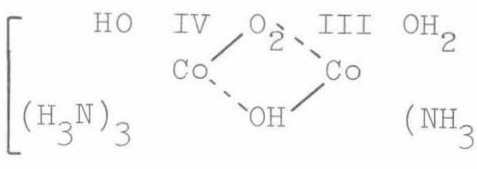
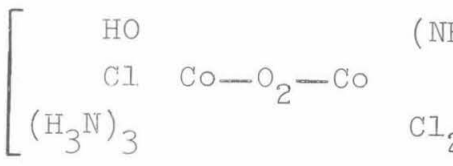
[1] R. J. Meyer and R. Jakobi, Ber. d. d. Chem. Ges. (1900) 33:2135; Z. F. Anorg. Chem. (1907) 27:364; L. Haitingef and V. von Lang, Annalen der Chemie (1907) 351:456

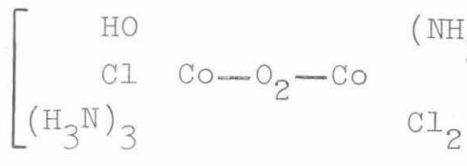
We thus arrive at the following formula for an expression of the constitution of the brown complex salts:



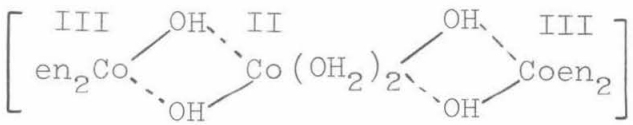
The behavior of the salts with concentrated hydrochloric acid also is in good agreement with this formulation. In the resulting tetrachloride only one of the chlorine atoms has an ionic character, as can be proven by the preparation of the nitrate. As expected, the chloride possesses the following constitutional formula:



The following constitutional formula corresponds to the nitrate:



M. Tetraethylenediamminediaquo-tetra-μ-hydroxo tricobalt (III,II,III) salts



The salts of this series result from the air oxidation of cobalt salt solutions containing ethylenediamine. They have already been described in an earlier paper.[2]

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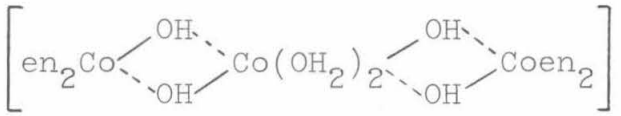
[2] Ber. d. d. Chem. Ges. (1907) 40:4426

Their constitution is given by the products of cold decomposition in hydrochloric acid and hydrobromic acid. Two molecules of cisdiaquo-diethylenediamine cobalt(III) salt and one molecule of cobalt(II) salt are formed. No chlorine or bromine is evolved in the decomposition. [41]



$$\left[en_2Co(OH)_2Co(OH_2)_2Co(OH)_2Coen_2\right]Cl_4 + 4HCl =$$

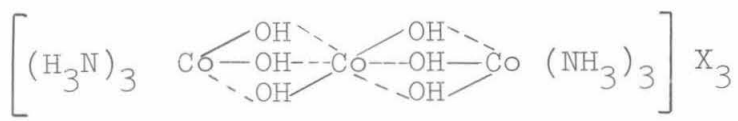
$$2\ [en_2Co(OH_2)_2]\ Cl_3 + CoCl_2 + 2H_2O\ .$$

The assumption that a divalent cobalt atom serves as the center of the molecule is most consistent with the ease with which the molecule is broken up. We have found that these compounds can be decomposed by briefly heating their aqueous solutions with ammonium chloride or ammonium bromide, giving chloroamminediethylenediamine cobalt and bromoamminediethylene-diamine cobalt salts:

$$\left[\begin{matrix} Cl \\ H_3N \end{matrix} Coen_2\right]X_2 \quad \text{and} \quad \left[\begin{matrix} Br \\ H_3N \end{matrix} Coen_2\right]X_2\ .$$

These singular decomposition reactions will be dealt with more thoroughly later.

N. Hexammine-hexa-μ-hydroxo tricobalt(III) salts



$$\left[(H_3N)_3\ Co(OH)_2Co(OH)_2Co\ (NH_3)_3\right]X_3$$

As a rule, in the preparation of the hexammine-tri-μ-hydroxo dicobalt(III) salts by various methods, a greenish-brown salt whose purification is generally very difficult as a secondary product is formed. Work with substantial amounts of these secondary products has now shown that a series of compounds is at hand which has six molecules of ammonia and three acid residues on three cobalt atoms. Decomposition with hydrochloric acid yields only dichloroaquotriammine cobalt(III) chloride, $[Cl_2Co\overset{OH_2}{(NH_3)_2}]$ Cl and a cobalt(II) salt, while chlorine gas is evolved. Since only triammine salts are obtained, the six ammonia molecules must be divided between two cobalt atoms, and the formation of the chlorine corresponding to the conversion of the cobalt atom without ammonia molecules from trivalent to divalent [42] is consistent with this. Since the complex radical is trivalent and no μ-amido bridges can be shown to be present, then the six cobalt valences must be satisfied by oxygen. This leads to the following constitutional formula for the salts:

$$[(H_3N)_3\ Co(OH)_3 \cdot Co(OH)_3 \cdot Co(NH_3)_3]\ X_3$$

The analytical data and the properties of the salts are in complete agreement with this formula. The latter also is in best accord with the salts being produced along with the hexammine-tri-μ-hydroxo dicobalt(III) salts since the $(NH_3)_3Co\overset{OH}{\underset{OH}{OH}}$ group participates in the formation of the latter. The existence of the hexa-μ-hydroxo tricobalt salts is important theoretically because it forcasts the existence of ammonia-free hexa-μ-hydroxo trimetal compounds, a new constitutional form for the basic trivalent metals.

O. Dodecammine-hexa-μ-hydroxo tetracobalt(III) salts and hexaethylene-diamine-hexa-μ-hydroxo tetracobalt(III) salts

$$\left[Co\left(\begin{matrix} OH \\ OH \end{matrix} Co(NH_3)_4 \right)_3 \right] X_6 \quad \text{and} \quad \left[Co\left(\begin{matrix} OH \\ OH \end{matrix} Co\ en_2 \right)_3 \right] X_6 \ .$$

The salts of these two series can be prepared from a great variety of tetrammine or bis{ethylenediammine}cobalt(III) salts. The details of the various preparation methods and the properties of these compounds have already been described.[1] The particulars

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[1] Ber. d. d. Chem. Ges (1907) 40:2103

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of the determination of their constitution have also been described earlier.

The cleavage products from reaction with hydrochloric acid were of particularly decisive importance for these determinations. Only tetrammine cobalt(III) and cobalt(II) resulted in this [43] decomposition, and in particular in the ratio of three molecules of the former to one molecule of the latter. Since the salts form neutral solutions, they can not be either aquo salts or hydroxo salts; and as all their acid residues are ionically bonded, the only possible constitutional expression for these compounds is the formula:

$$\left[Co\left(\begin{matrix} OH \\ OH \end{matrix} CoA_4 \right)_3 \right] X_6 \ .$$

EXPERIMENTAL

I. Decammine-μ-amido dicobalt(III) salts

$$\left[(H_3N)_5Co{-}NH_2{-}Co(NH_3)_5\right] X_5 .$$

The properties of the salts of this series have been thoroughly described in an earlier paper.[1] Consequently, we will content

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[1] Ber. d. d. Chem. Ges. (1908) 41)3912

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ourselves with describing a new method of preparation for this series, using chloroaquooctammine-μ-amido dicobalt(III) chloride,

$$\left[\begin{matrix} & Cl \\ (H_3N)_4 & \end{matrix} Co{-}NH_2{-}Co \begin{matrix} OH_2 \\ (NH_3)_4 \end{matrix}\right] Cl_4 ,$$

as the starting material.

If a freshly prepared solution of this salt is treated with concentrated nitric acid, a grey-violet nitrate precipitates out which on the basis of its composition is chloronitratooctammine-μ-amido dicobalt nitrate.

$$\left[\begin{matrix} & Cl \\ (H_3N)_4 & \end{matrix} Co{-}NH_2{-}Co \begin{matrix} NO_3 \\ (NH_3)_4 \end{matrix}\right] (NO_3)_4 .$$

If the well dried salt is then covered with liquid ammonia, it dissolves immediately, giving a brown solution. After the ammonia is evaporated, the residue is covered with water and heated in a water bath until most of it has dissolved. The [44]

undissolved residue is filtered from the hot solution and then recrystallized from boiling dilute acetic acid solution. Long, needle-like, brilliant violet crystals of the nitrate of the decammine-μ-amido dicobalt(III) series are formed on cooling. Good yields are obtained if much liquid ammonia is used and if it is allowed to evaporate slowly.

To obtain analytically pure nitrate the product must be reprecipitated from aqueous nitric acid solution several times as it still contains chloride. The last traces of chloride are removed with a little silver nitrate. The nitrate purified in this way gave the following analysis:

0.0721 g gave 0.0366 g $CoSO_4$

	calc. for $[Co_2(NH_3)_{10}NH_2](NO_3)_5$	found
Co	19.21%	19.27%

II. Octammine-μ-amido-μ-hydroxo dicobalt(III) series and its derivatives

The preparation and properties of the octammine-μ-amido-μ-hydroxo dicobalt(III) salts have already been described.[1]

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[1] Ber. d. d. Chem. Ges. (1907) 40:4605

Consequently, only the series that have been derived from this basic series will be described here.

A. Chloroaquooctammine-μ-amido dicobalt(III) series

(F. Salzer)

$$\left[\begin{matrix} H_2O \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Cl \\ (NH_3)_4 \end{matrix}\right] X_4 \ .$$

Already in the first investigation of the octammine-μ-amido-μ-hydroxo dicobalt(III) salts,[2] a great excess of chlorine was

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[2] Z. f. anorg. Chem. (1899) 19:125

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found when the chloride was analyzed, namely 34.3% instead of 28%. It could not be ruled out that this excess chlorine content might result from the presence of a more chlorine rich salt. To determine the reason for the high chlorine content, a renewed [45] investigation was undertaken which resulted in the discovery of a chloro series that is a derivative of the octammine-μ-amido-μ-hydroxo dicobalt(III) series. Octammine-μ-amido-μ-sulfato dicobalt(III) nitrate, which can be obtained from Vortmann's sulfate,[1] is the most convenient starting material for the

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[1] Ber. d. d. Chem. Ges. (1907) 40:4610

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preparation of this new series. This salt is converted into the chloride of the chloro series by the following method, which has been worked out on the basis of a great number of experiments.

1. Chloride: $\left[\begin{matrix} H_2O \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Cl \\ (NH_3)_4 \end{matrix}\right] Cl_4 \cdot 4H_2O$

Portions of 10 g of crude sulfato nitrate in Erlenmeyer flasks are each covered with 150 ml of concentrated hydrochloric acid. These are allowed to stand, loosely stoppered, at room temperature. The nitrate dissolves almost completely initially and gradually a grey-brown salt precipitates out. The reaction is complete after 24 hours if care has been taken to agitate the solution efficiently. The crystals are then filtered off and spread on a clay plate to remove the acid adhering to them. For purification, the crude salt is dissolved in ice-cold water (20 g salt in ca. 400 ml water), the undissolved salt is filtered out as quickly as possible, and the chloride is reprecipitated by the addition of 140 ml of ice-cold hydrochloric acid. Generally, slightly better than 4 g of pure chloride is obtained from 10 g of nitrate.

The chloride thus prepared forms brown-violet, needle-like crystals that are very soluble in water, but insoluble in organic solvents. The aqueous solution is acidic. If concentrated solutions are allowed to stand for some time, fine prismatic red-brown crystals of the less soluble octammine-μ-amido-μ-hydroxo dicobalt(III) chloride separate out, the salt being formed according to the following reaction: [46]

$$\left[\begin{matrix} H_2O \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Cl \\ (NH_3)_4 \end{matrix}\right] Cl_4 = \left[(H_3N)_4Co\begin{matrix} NH_2 \\ OH \end{matrix}Co(NH_3)_4\right] Cl_4 + HCl$$

0.2712 g gave 0.3672 g AgCl

0.5816 g lost 0.076 g water after being dried for 13 days to constant weight in vacuum over P_2O_5 .

	calc. for $Co_2(NH_3)_8NH_2OHCl_5 \cdot 4H_2O$	found
Co	--	--
Cl	32.95%	33.00%
$4H_2O$	13.3	13.06

The chloride is completely cleaved into pentammine and tetrammine cobalt(III) salts by heating for a long period in concentrated hydrochloric acid. This is done by mixing a saturated solution of the chloride with half of its volume of concentrated hydrochloric acid and heating it in a water bath until the initially precipitated salt redissolves. The solution is then cooled and the precipitated salt filtered off. By heating this salt with half-saturated* hydrochloric acid,

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*See Translator's note on p. 49

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chloropentammine cobalt(III) chloride goes into solution. This may be reprecipitated in pure form by cooling.

0.1093 g gave 0.0675 g $CoSO_4$

0.1044 g gave 26.2 ml Nitrogen gas

0.1013 g gave 0.1742 AgCl

	calc. for $Co(NH_3)_5Cl_3$	found
Co	23.50%	23.54%
N	28.00	27.90
Cl	42.38	42.52

A freshly prepared, aqueous, saturated solution of chloro-aquococtammine-μ-amido dicobalt(III) chloride has the following behavior with the reagents listed below.

Platinic chloride gives, after some time, a precipitate consisting of shiny copper-bronze colored flakes. The formation of the precipitate can be speeded up by scratching the glass [47] wall of the container with a glass rod.

Mercuric chloride rapidly gives a precipitate of small, glittering, crimson red crystals which are nearly insoluble in water.

If potassium iodide is added until the solution is saturated an amorphous, brown-red, powdery precipitate is formed which is very soluble in water.

2. Sulfate: $\begin{bmatrix} H_2O & & Cl \\ (H_3N)_4 & Co—NH_2—Co & (NH_3)_4 \end{bmatrix} (SO_4)_2 \cdot 1H_2O$

If a freshly prepared solution of the chloride is treated with dilute sulfuric acid, a pale reddish-violet crystalline

precipitate is formed quantitatively. The precipitation is so complete that the liquid above the precipitate is only weakly rose colored. Because of its insolubility in water, the sulfate, in the form of an aqueous suspension, is very stable to heating, while the soluble salts of chloro series quickly transform into octammine-μ-amido-μ-hydroxo dicobalt(III) salts by giving up hydrochloric acid.

For the analysis the salt was washed with water, alcohol and ether and dried over concentrated sulfuric acid.

0.1087 g gave 0.0637 g $CoSO_4$

0.1147 g gave 25 ml Nitrogen at 21.5° and 725.5 mm pressure

0.1272 g gave 0.1117 g $BaSO_4$

0.0013 g H_2O lost after heating 0.4104 g at 105° for 2 hours

	calc. for $Co_2N_9H_{28}S_2O_9Cl \cdot H_2O$	found
Co	22.10%	22.30%
N	23.70	23.47
Cl	6.60	6.30
SO_4	36.60	36.16
$1H_2O$	3.38	3.20

Only the water not bound to the radical is lost on heating.

3. Dithionate: $\left[\begin{matrix} H_2O \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Cl \\ (NH_3)_4 \end{matrix}\right] (S_2O_6)_2$ [48]

Since the dithionate is, like the sulfate, insoluble in water, it precipitates out immediately in the form of a voluminous,

grey-violet crystalline precipitate when sodium dithionate is added to a freshly prepared solution of the chloride.

When moist, the salt has a bright bronze-like luster. After being dried over concentrated sulfuric acid, the salt has the formula given above. If it is heated at 115° for eight hours, it loses its water of constitution but immediately recovers this one molecule of water on cooling in the air. This behavior is very peculiar and is undoubtedly worthy of further investigation.

0.1077 g gave 0.0512 g $CoSO_4$

0.1044 g gave 18.4 ml Nitrogen at 18° and 726 mm pressure

0.1410 g gave 0.031 g AgCl

0.1400 g lost 0.0042 g at 155°

	calc. for $Co_2N_9H_{28}S_4O_{13}Cl$	found
Co	18.30%	18.10%
N	19.60	19.40
Cl	5.60	5.43
H_2O	2.80	3.00

III. Chlorothiocyanatooctammine-μ-amido dicobalt(III) thiocyanate

$$\left[\begin{matrix} NCS \\ (NH_3)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Cl \\ (NH_3)_4 \end{matrix}\right] (SCN)_3 \ .$$

This salt was obtained by treating a completely saturated solution of the chloride with a saturated ammonium thiocyanate solution or with solid ammonium thiocyanate. The thiocyanate, which is more soluble than the chloroaquochloride, precipitates

as small, brown-red, strongly reflecting crystals. The salt was washed with alcohol and ether and dried for twenty-four hours over conc. H_2SO_4 before analysis.

0.1113 g gave 0.0645 g $CoSO_4$ [49]

0.1111 g gave 0.0648 g $CoSO_4$

0.0974 g gave 30 ml Nitrogen at 22.5° and 731 mm pressure

0.0987 g gave 31.2 ml Nitrogen at 22.0° and 724 mm pressure

0.1921 g gave 0.053 g AgCl

	calc. for $Co_2N_{13}H_{26}C_4S_4Cl$	found	
Co	21.90%	22.05%	22.20%
N	33.72	33.40	33.80
Cl	6.60	6.82	

The salt was heated with fuming nitric acid in a bomb tube for the chlorine determination. The resulting mixture of silver chloride and silver nitrate was repeatedly washed with dilute nitric acid to remove the latter component.

IV. Chloronitratooctammine-μ-amido dicobalt(III) nitrate

$$\left[\begin{matrix} Cl \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} NO_3 \\ (NH_3)_4 \end{matrix} \right] (NO_3)_3 \cdot$$

Chloroaquooctammine-μ-amido dicobalt(III) chloride is used as the starting material for the preparation of this salt.

Three grams of chloroaquooctammine-μ-amido dicobalt(III) chloride are dissolved in 50 ml of ice-cold water, and the

filtered solution is then mixed with 15 ml of concentrated nitric acid. A red-violet precipitate (probably the corresponding aquo salt) forms initially but very quickly takes on a brown-violet color. The precipitate is filtered off and washed with dilute nitric acid (1:1). Yield: 2.5 grams.

The salt consists of needlelike brown-violet crystals that are very soluble in water. When silver nitrate is added to a freshly prepared aqueous solution of the nitrate, there is no immediate effect but after a while the solution becames opalescent, and gradually a plentiful precipitate of silver chloride is formed. The silver chloride precipitates very quickly if the solution is heated.

0.1230 g gave 0.0692 g $CaSO_4$
0.1148 g gave 0.0644 g $CoSO_4$
0.1670 g gave 0.0428 g AgCl*
0.1886 g gave 0.0470 g AgCl

	calc. for $Co_2N_{13}H_{26}ClO_{12}$	found	
Co	21.34%	21.40%	21.34%
Cl	6.40	6.33	6.16

[50]

*Translator's note: An apparent typesetting error gives the sample weight as 0.0167 g in the original.

If dilute sulfuric acid is added to a warm aqueous solution of the nitrate, octammine-μ-amido-μ-hydroxo dicobalt(III) sulfate precipitates out.

V. Bromoaquooctammine-μ-amido dicobalt(III) salts

$$\left[\begin{matrix} Br \\ (NH_3)_4 \end{matrix} Co{-}NH_2{-}Co \begin{matrix} OH_2 \\ (NH_3)_4 \end{matrix}\right] Br_4 \cdot$$

A. Bromide

The preparation of this salt begins with octammine-μ-amido-μ-hydroxo dicobalt sulfate. By covering this sulfate with concentrated hydrobromic acid it is immediately converted into a brown violet mass which is then suction filtered and triturated twice more with concentrated hydrobromic acid. The product is then washed acid free with alcohol, dried and dissolved in a minimum of ice-cold water. Any violet salt present is quickly filtered off and the solution is then treated with concentrated hydrobromic acid, giving the desired bromide as dark brown, flat, needle-like crystals which are filtered off, washed acid-free with alcohol and dried over sulfuric acid.

I. 0.0970 g gave 0.0435 g $CoSO_4$
0.1010 g gave 16.8 ml Nitrogen at 19° and 718 mm pressure
0.1018 g gave 0.1353 g AgBr

II. 0.0917 g gave 0.0410 g $CoSO_4$
0.1039 g gave 0.1387 g AgBr

	calc. for $Co_2N_9H_{28}OBr_5$	found I	found II
Co	16.71%	17.07%	17.01%
N	17.84	17.94	--
Br	56.65	56.55	56.78

The salt is quite soluble in water. Aqueous solutions are acidic and initially reddish-brown in color. On standing, they become a crimson red color, and red prismatic crystals of [51] octammine-μ-amido-μ-hydroxo dicobalt(III) bromide precipitate out. The latter salt is converted back into bromoaquooctammine-μ-amido dicobalt(III) bromide on standing in concentrated hydrobromic acid.

B. Sulfate: $\left[\begin{matrix} H_2O \\ (H_3N)_4 \end{matrix} Co—NH_2—Co \begin{matrix} Br \\ (NH_3)_4 \end{matrix} \right] (SO_4)_2 \cdot H_2O$

In order to demonstrate that one bromine atom in the bromide just described is not ionically bonded, this salt was converted to the sulfate. Completely pure sulfate could not be obtained, since the bromo bromide transforms extraordinately quickly into octammine-μ-amido-μ-hydroxo dicobalt(III) bromide in aqueous solution. At any rate, the result of the experiment was such that the non-ionic character of the single bromine atom cannot be doubted. The experiment was carried out in the following way. The bromo bromide was placed in a suction filter, covered with some ice-cold water, and the resulting solution was allowed to run immediately into dilute (1:1) sulfuric acid. Fine, dark-brown crystals of the sulfate are formed immediately, the analysis of which gave the following results:

0.1002 g gave 0.0298 g AgBr

0.0994 g gave 0.0864 g $BaSO_4$

	calc. for $Co_2N_9H_{28}BrS_2O_9 \cdot 1H_2O$	found
Br	14.15%	12.65%
S	11.29	11.87

The sulfate is almost completely insoluble in water.

VI. Octammine-μ-amido-μ-sulfato dicobalt(III) salts

$$\left[(H_3N)_4Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(NH_3)_4\right]X_3 \cdot$$

This series, which was first investigated in association with A. Baselli, has previously been designated as the octammine-μ-imido-μ-hydrosulfato dicobalt(III) series.[1] At that time the

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[1]Zeitschr. f. anorg. Chem. (1898) 16:731

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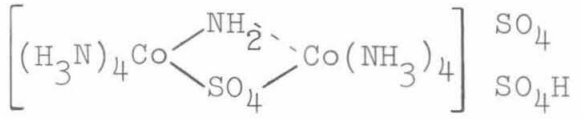
violet nitrate obtained from Vortmann's sulfate was used as the [52]
starting material for the preparation of these salts. However, this crude nitrate always contains small amounts of other salts thus making the preparation of analytically pure salts of this series from it of considerable difficulty. It is much more convenient instead to start with pure octammine-μ-amido-μ-hydroxo salts and to heat them in solution with some sulfuric acid. The pale red sulfate that initially precipitates out redissolves with the formation of a bright red-violet solution. The salts can then be precipitated from this solution by using the appropriate reagents.

The salts prepared by this method are described below.

A. Acid sulfate: 

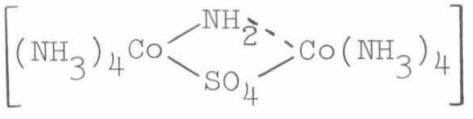
Three grams of octammine-μ-amido-μ-hydroxo dicobalt chloride are covered with 10 ml of water and 2 grams of concentrated sulfuric acid and the resulting mixture heated over an open flame until a clear violet solution is obtained. On cooling, purple-violet prismatic flakes crystallize out, forming a slurry which is filtered and dried. This crude product can be recrystallized from dilute sulfuric acid. The dry product is a slightly lustrous, brown-violet, crystalline powder. The analysis has shown that this is an acid sulfate of the sulfato series.

0.1446 g gave 0.0785 g $CoSO_4$

0.1446 g gave 0.1767 g $BaSO_4$

	calc. for $Co_2N_9H_{27}S_3O_{12}$	found
Co	20.65%	20.66%
S	16.80	16.78

The acid sulfate investigated by Baselli contained one molecule of water of crystallization; it is questionable, however, whether or not that salt was completely pure.

B. Bromide:  [53]

25 ml of water and 20 ml of dilute sulfuric acid (1:3) are added to 1 gram of octammine-μ-amido-μ-hydroxo dicobalt(III) bromide, and the mixture is heated. A violet solution is obtained which is cooled and then treated with 15 ml of concentrated hydrobromic acid. After a short time the bromide has precipitated in the form of red-violet needle-like crystals. The salt is purified by dissolving it in water and reprecipitating it by the addition of hydrobromic acid.

The air dried salt gave the following results on analysis:

0.1476 g gave 0.0735 g $CoSO_4$

0.1385 g gave 0.1257 g AgBr

	calc. for $Co_2N_9H_{26}SO_4Br_3 \cdot H_2O$	found
Co	18.91%	18.94%
Br	38.46	38.62

The salt loses its water of crystallization on heating at 110°.

C. Nitrate: $\left[(NH_3)_4Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_3$

The nitrate is prepared from the acid sulfate. The latter is first dissolved in cold water, in which it is very slightly soluble, and then treated with nitric acid. The nitrate immediately settles out as small violet red crystals, which can be purified by recrystallization from aqueous solution by addition of nitric acid.

0.1532 g gave 0.0859 g $CoSO_4$

	calc. for $Co_2N_{12}H_{26}SO_{13}$	found
Co	21.50%	21.31%

The nitrate is slightly soluble in water and almost insoluble in nitric acid solutions.

Other salts of the sulfato series were not prepared from the octammine-μ-amido-μ-hydroxo series, since they have already been [54] obtained by other methods.

VII. Octammine-μ-amido-μ-nitrito dicobalt(III) salts

by F. Salzer and M. Pieper

$$\left[(H_3N)_4Co\begin{matrix}NH_2\\NO_2\end{matrix}Co(NH_3)_4\right]X_4 .$$

The nitrate, chloride and sulfate of this series have been described previously as hydronitritooctammine-μ-imido dicobalt salts.[1] Since then, their constitution has been completely

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[1] Zeitsch r. f. anorg. Chem. (1898) 16:156

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clarified and the series has been thoroughly investigated. They form one of the most stable of the presently known polynuclear cobalt ammine series.

Various salts can be chosen as the starting material in the preparation of the salts of this series, namely, octammine-μ-amido-μ-hydroxo dicobalt(III) salts, chloroaquooctammine-μ-amido

dicobalt(III) salts, or octammine-μ-peroxo dicobalt(III,IV) salts.

Since the nitrate of this series is very nearly insoluble in nitric acid solutions it is the most suitable for the isolation of the series.

A. Preparation from octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate

The green nitrate is covered with a little water and the resulting paste is treated with concentrated nitric acid. Concentrated sodium nitrite solution is added dropwise to the mixture with constant stirring. Nitric acid must always be present in excess. The green nitrate initially turns dirty brown and finally becomes a fine orange yellow. When no more dark traces can be seen, the crystals are filtered off with a suction filter and then are recrystallized from nitric acid solution. The yield of nitrito nitrate is roughly equal to the weight of green nitrate that was used.

B. Preparation from octammine-μ-amido-μ-hydroxo dicobalt(III) chloride [55]

A freshly prepared concentrated aqueous solution of the chloride is acidified with acetic acid. On heating and adding sodium nitrite to the solution, there is a rapid change in color to yellow-brown. Once this occurs, the solution is cooled and treated with nitric acid, yielding in a short time a thick slurry of crystals which are filtered off and recrystallized from nitric acid solution.

C. Preparation from chloroaquooctammine-μ-amido dicobalt(III) chloride

A concentrated, freshly prepared solution is treated with sodium nitrite and the solution heated slightly in a water bath. The color quickly changes from brown-red to orange. As soon as this has occurred, concentrated nitric acid is added to the solution, whereupon a slurry of orange colored needle-like crystals of the octammine-μ-amido-μ-nitrito dicobalt(III) nitrate precipitates out.

D. Nitrate: $\left[(H_3N)_4Co\begin{smallmatrix}NH_2\\NO_2\end{smallmatrix}Co(NH_3)_4\right](NO_3)_4 \cdot 1H_2O$

The salt prepared according to one of the above methods is recrystallized from warm aqueous nitric acid solution, forming clusters of orange colored, flat, reflective needles up to 1 cm long.

Analysis of the salt dried over H_2SO_4:

0.0933 g gave 0.0503 g $CaSO_4$

0.1000 g gave 30.6 ml Nitrogen at 17° and 723 mm pressure

0.1298 g gave 0.0542 g H_2O

	calc. for $Co_2N_{14}H_{26}O_{14} \cdot H_2O$	found
Co	20.20%	20.44%
N	33.59	33.69
H	--	4.70

Analysis of the salt dried to constant weight at 100°:

0.0893 g gave 0.0500 g $CoSO_4$

0.0988 g gave 31.7 ml Nitrogen at 20.5° and 721 mm pressure

	calc. for $Co_2N_{14}H_{26}O_{14}$	found
Co	20.90%	21.00%
N	34.70	34.68

[56]

Since one molecule of acid can be split off from some μ-amido-μ-sulfato dicobalt(III) salts under certain circumstances to form μ-imido salts, a similar reaction was attempted here. But this could not be achieved either by mixing with ammonia or by treatment of a solution of the nitrate with ammonia and subsequent precipitation with alcohol. Only unchanged nitrate resulted, as shown by the analysis.

0.1124 g gave 0.0599 g $CoSO_4$

0.1031 g gave 32.3 ml Nitrogen at 20° and 720 mm pressure

	calc. for $Co_2N_{14}H_{26}O_{14} \cdot 1H_2O$	found
Co	20.20%	20.30%
N	33.59	33.90

A peculiar property of the nitrate was observed in an attempt to split off one molecule of acid with pyridine. The salt which crystallizes out of a solution containing pyridine contains one molecule of pyridine for each molecule of salt, but this pyridine is not involved in the complex itself. This pyridine-containing compound was prepared as follows: A few drops of pyridine were added to a warm concentrated aqueous solution of octammine-μ-

amido-μ-nitrito dicobalt(III) nitrate. On cooling, a flesh-colored salt crystallized in the form of radiating glittering flakes having a much paler color than the original nitrate. This was washed with alcohol and ether and dried in a desiccator over H_2SO_4 for analysis.

0.1907 g gave 0.0920 g $CoSO_4$
0.1768 g gave 0.0832 g $CoSO_4$
0.1369 g gave 0.0653 g $CoSO_4$
0.0754 g gave 22.7 ml Nitrogen at 21.0° and 723 mm pressure
0.0516 g gave 15.6 ml Nitrogen at 19.5° and 725 mm pressure
0.0429 g gave 13.1 ml Nitrogen at 21.0° and 722 mm pressure

	calc. for $Co_2N_{14}H_{26}O_{14}$ + Py	found			[57]
Co	18.38%	18.43%	18.11%	18.15%	
N	32.71	32.45	32.95	32.91	

The salt containing pyridine has a mealy texture but does not have any pyridine odor. It is very soluble in water. The aqueous solution smells strongly of pyridine and, if dilute sulfuric acid is added to it, pyridine free octammine-μ-amido-μ-nitrito dicobalt(III) sulfate is immediately formed, as is shown by the following analysis:

0.1176 g gave 0.0670 g $CoSO_4$
0.1740 g gave 0.0998 g $CoSO_4$
0.1526 g gave 0.0876 g $CoSO_4$
0.0946 g gave 22.6 ml Nitrogen at 23° and 718 mm pressure
0.1789 g gave 0.1534 g $BaSO_4$

	calc. for $Co_2N_{10}H_{26}O_{10}S \cdot 2H_2O$	found		
Co	21.69%	21.68%	21.83%	21.85%
N	25.73		25.34	
S	11.76		11.78	

E. Chloride: $\left[(H_3N)_4Co\begin{matrix}NH_2\\NO_2\end{matrix}Co(NH_3)_4\right]Cl_4 \cdot H_2O$

If the nitrate is covered with a little concentrated hydrochloric acid and stirred with a spatula, a dark orange solution is quickly formed. Needle-like crystals soon appear, however, and the whole solution shortly solidifies into a crystal slurry. This product is again treated with hydrochloric acid and recrystallized from an aqueous hydrochloric acid solution, giving rhombic plates or columnar prisms.

The chloride can also be prepared from the sulfate. The sulfate initially dissolves on being stirred into concentrated hydrochloric acid and the resulting solution quickly solidifies into a thick slurry of crystals which can be dissolved by the addition of a little water. After the remaining undissolved sulfate has been filtered out, beautiful dark-brown prismatic crystals of the pure chloride form.

I. Preparation from the nitrate [58]

0.1136 g gave 0.0730 g $CoSO_4$

0.1082 g gave 0.1280 g AgCl

0.1000 g gave 27.0 ml Nitrogen at 19.5° and 715 mm pressure

II. Preparation from the sulfate

0.1189 g gave 0.0769 g $CoSO_4$

0.0911 g gave 24.8 ml Nitrogen at 25.5° and 727 mm pressure

	calc. for $Co_2N_{10}O_2H_{26}Cl_4 \cdot 1H_2O$	found I	found II
Co	24.80%	24.61%	24.58%
N	29.42	29.05	29.37
Cl	29.84	29.27	--

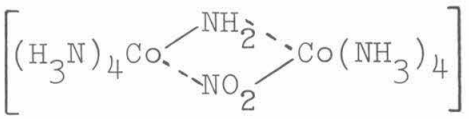
The chloride is very soluble in water and can be reprecipitated by the addition of hydrochloric acid. In addition to the chloride described above, which contains one molecule of H_2O, a hydrate containing four molecules of H_2O also exists. This was discovered in the attempt to split off one molecule of HCl with pyridine.

When a warm solution of the chloride that has been treated with pyridine is cooled, bright red-brown rhombohedral prisms separate out. These crystals have a color that is somewhat brighter than that of the starting material.

0.1108 g gave 0.0650 g $CoSO_4$

0.1026 g gave 24.8 ml Nitrogen at 19.5° and 716 mm pressure

	calc. for $Co_2N_{10}O_2H_{26}Cl_4 \cdot 4H_2O$	found
Co	22.30%	22.33%
N	26.46	26.05

F. Bromide:  $Br_4 \cdot 3H_2O$

For the preparation of this salt the corresponding sulfate was used as the starting material. A stoichiometric amount of barium bromide was added to a sulfate solution and the mixture was acidified with a few drops of hydrobromic acid and heated in a water bath. Barium sulfate precipitated out and the bromide dissolved. The solution was filtered and cooled and hydrobromic acid added to it until no more salt precipitated. The remaining mother liquor was only weakly orange colored.

By slowly concentrating an aqueous solution of the bromide by [59] evaporation in a desiccator, beautifully formed, frequently inter-penetrating, brown-red rhombohedral prisms up to 1/2 cm long can grow in a few days. On the other hand, if a concentrated aqueous solution of the bromide is slowly cooled in a water bath, regular rhombohedral plates result.

These latter were analyzed:

I. 0.1093 g gave 0.0495 g $CoSO_4$

0.1466 g gave 0.1596 g AgBr

0.1008 g gave 19.0 ml Nitrogen at 19° and 707.5 mm pressure

The analysis of the brown-red crystals gave:

II. 0.1042 g gave 0.0467 g $CoSO_4$

0.0919 g gave 0.0409 g $CoSO_4$

0.1123 g gave 21.9 ml Nitrogen at 22° and 724 mm pressure

	calc. for $Co_2N_{10}O_2Br_4H_{26} \cdot 3H_2O$	found I	found II
Co	17.08%	16.90%	17.06% 16.94%
N	20.34	20.50	20.55
Br	46.32	46.33	--

The water-free salt can be obtained by heating at 105° for several hours until constant weight is reached.

0.1156 g gave 0.0562 g $CoSO_4$

0.1152 g gave 23.38 ml Nitrogen at 18° and 766 mm pressure

	calc. for $Co_2N_{10}O_2Br_4H_{26}$	found
Co	18.50	18.50
N	22.13	22.32
H_2O	7.80	7.60

G. <u>Iodide</u>: $\left[(H_3N)_4Co\begin{matrix}NH_2\\NO_2\end{matrix}Co(NH_3)_4\right] I_4 \cdot H_2O$

The iodide precipitates as a brown-red micro-crystalline powder from a cold aqueous solution of the nitrate on addition of potassium iodide. It can be purified by reprecipitating it with potassium iodide from aqueous solution. Very fine crystals (large, dark red prisms) are obtained by letting an aqueous solution of the iodide evaporate in a desiccator.

0.1400 g gave 0.0510 g $CoSO_4$ [60]

0.0903 g gave 14.0 ml Nitrogen at 22.5° and 722 mm pressure

	calc. for $Co_2N_{10}H_{26}O_2I_4 \cdot H_2O$	found
Co	14.08%	13.86%
N	16.70	16.69

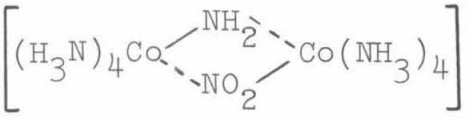
An iodide tetrahydrate is obtained by recrystallizing the salt from an aqueous solution containing pyridine.

The tetrahydrate differs in appearance from the monohydrate by having a somewhat brighter color. Its crystals are rhombohedral plates.

0.1284 g gave 0.0448 $CoSO_4$

0.0952 g gave 13.2 ml Nitrogen at 19° and 724 mm pressure

	calc. for $Co_2N_{10}H_{26}O_2I_4 \cdot 4H_2O$	found
Co	13.25	13.28%
N	15.71	15.82

H. Sulfate:  $(SO_4)_2 \cdot 2H_2O$

When dilute sulfuric acid is added to a solution of the nitrate, the insoluble sulfate separates out as dull orange small crystals.

0.0976 g gave 0.0558 g $CoSO_4$

0.1396 g gave 0.0797 g $CoSO_4$

0.4114 g gave 0.3530 g $BaSO_4$

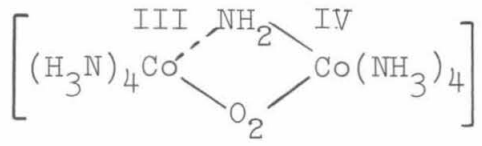
0.2487 g gave 0.2137 g $BaSO_4$

	calc. for $Co_2N_{10}H_{26}S_2O_{12} \cdot 2H_2O$	found	
Co	21.69%	21.76%	21.73%
S	11.76	11.79	11.85

The sulfate dissolves in concentrated sulfuric acid, forming a dark red-yellow solution from which it may be reprecipitated by dilution with water. It can similarly be dissolved in concentrated

hydrochloric acid and reprecipitated after some time as the chloride by diluting the solution.

VIII. Octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts [61]



Vortmann's Sulfate, whose preparation and processing have been described in an earlier publication,[1] is used as the

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[1]Ber. d. d. Chem. Ges. (1907) 40:4609

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starting material for this series of compounds. I first studied this series some time ago in association with F. Beddow.[2] Since

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[2]Zeitschr. f. anorg. Chem. (1898) 16:129

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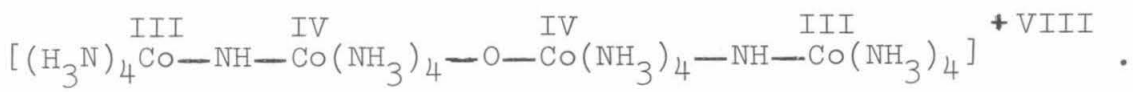
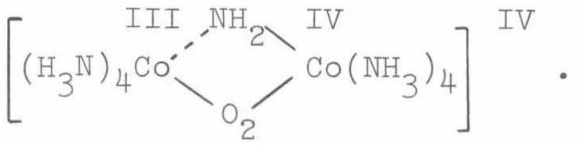
it could not at that time be determined how many tetravalent cobalt atoms are contained in the complex radical of these polynuclear cobalt ammines or how much excess oxygen is present or whether or not the two cobalt atoms are bonded together through an imido group or an amido group, the following formula for the complex radical was advanced:



This contained two trivalent cobalt atoms situated at the ends and two tetravalent cobalt atoms in the middle. The series was designated as the μ-oxo-bis{octammine-μ-imido dicobalt(III)} series. Since then a renewed investigation carried out by my assistant Dr. A. Grun and myself has shown that the complex radical has a substantially simpler structure consisting of one trivalent and one tetravalent cobalt atom which are bound together by one amido group and one peroxo group. Each cobalt atom also has four ammonia molecules bonded to it. The structure corresponds to the following constitutional formula:



The salts are thus designated as <u>octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts</u>. The facts established as a result of [62] the renewed work on this series are summarized below.

A. <u>Determination of the constitution</u>

That it is possible to convert this series into octammine-μ-amido-μ-hydroxo dicobalt(III) salts is of decisive importance for the determination of its constitution. This reduction can be carried out in a simple way as follows.

Fifteen ml of water and 2.5 ml of glacial acetic acid are poured over 3 g of the green nitrate. This is then treated with 3 g of potassium iodide in 5 ml of water, and 1 g of thiosulfate. The solution, which at first has a deep brown color because of the iodine, takes on a red color and a red precipitate forms

which is filtered off. Some red bromide remaining in solution can still be precipitated by the addition of ammonium bromide. The solid red salt is ground with 5 g of ammonium bromide and a little water three times to form a well dispersed slurry. After the third operation, the originally very slightly soluble salt is easily dissolved in water. The resulting solution is then filtered and the salt reprecipitated by the addition of ammonium bromide. The collected bromide precipitate is then purified by one more reprecipitation from aqueous solution. The yield of red bromide, which has been shown to be <u>octammine-μ-amido-μ-hydroxo dicobalt(III) bromide</u>, is about 2 g.

0.1253 g gave 0.0577 g $CoSO_4$

0.1808 g gave 0.1995 g AgBr

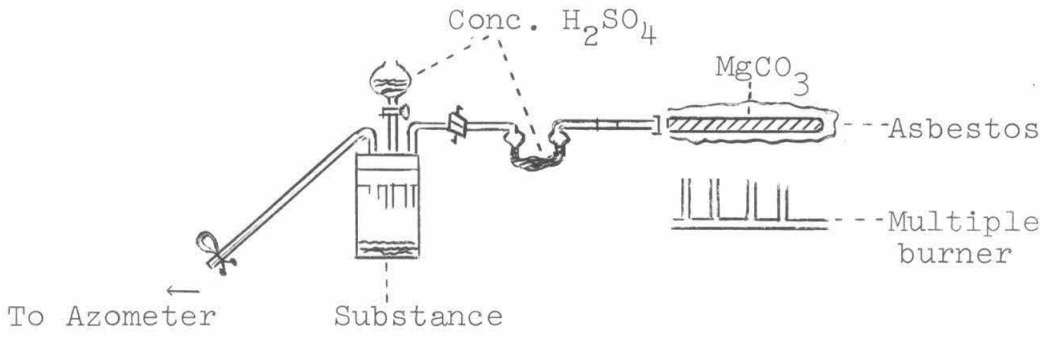
	calc. for $Co_2N_9H_{27}OBr_4 \cdot 4H_2O$	found
Co	17.38%	17.53%
Br	47.10	46.97

This demonstrates that the green series is related to the <u>octammine-μ-amido-μ-hydroxo dicobalt(III) series</u>.

It then remained to be determined whether only some or all of the cobalt of our series is tetravalent. This was successfully determined only after a great many fruitless attempts. At first we attempted to measure the amount of molecular oxygen evolved [63] when the salts were heated with water. The excess of oxygen over that expected for divalent cobalt was titrimetrically determined from the residual oxide. The results were inconclusive, primarily because the experimental errors were too great because

of the relatively voluminous apparatus. We then attempted to titrimetrically determine the amount of oxygen actively involved in the oxidation of hydrogen iodide when the salt is reduced with this substance. This similarly gave poor results because, as could be shown, some of the oxygen was liberated as gaseous oxygen and therefore did not participate in the oxidation of the hydrogen iodide. We then finally discovered a method that has proved to be completely reliable in other cases as well.

To be sure, this method has only limited applicability since the determination can only be carried out with sulfates, but the results are completely satisfactory. It is based upon the fact that the cobalt in the sulfates of the cobalt ammines is smoothly converted into cobalt(II) sulfate on being heated with concentrated sulfuric acid. A reduction of the trivalent and tetravalent cobalt atoms to divalent takes place and the [64] equivalent amounts of gaseous nitrogen and oxygen corresponding to these valence changes are evolved. With the simple ammonia-rich cobalt ammines only nitrogen is formed while with the polynuclear cobalt ammines, especially those containing tetravalent cobalt, oxygen is evolved at the same time. From the amount of gases formed, information is obtained about the reactions by which the conversion into cobalt sulfate has taken place. This is shown below. The experiment was carried out using the following apparatus:



The weighed salt was placed in a small beaker, ($3\frac{1}{2}$ cm high, $2\frac{1}{2}$ cm in diameter) and the air was then completely replaced with carbon dioxide. Concentrated sulfuric acid was added by means of a dropping funnel, heat applied, and the gases were collected in an ordinary nitrogen determination apparatus. The oxygen was absorbed from the gas mixture by using alkaline pyrogallol solution; the remainder was nitrogen.

The procedure corresponds to that customarily used for the determination of nitrogen in organic compounds and consists of the following operations:

1. Forcing the air from the apparatus with CO_2, which is generated from magnesium carbonate or sodium bicarbonate.

2. Connecting the apparatus used for the nitrogen determination and allowing the sulfuric acid to flow in from the dropping funnel.

3. Heating the beaker until the sulfuric acid solution takes on a pure blue color and rose colored cobalt sulfate has precipitated.

4. Determining the ratios of oxygen and nitrogen by means of alkaline pyrogallol solution.

Below are the results obtained with the help of this method for a few simple cobalt ammines.

1. Hexammine cobalt(III) sulfate $[Co(NH_3)_4]_2\ (SO_4)_3$

0.4010 g gave 5.10 ml Nitrogen at 17° and 718 mm pressure

calc. N 1.33% found N 1.40%

2. Hydroxoaquotetrammine cobalt(III) sulfate $\left[\begin{matrix}HO\\H_2O\end{matrix}\ Co(NH_3)_4\right]\ SO_4 \cdot 1H_2O$ [65]

0.4301 g gave 6.0 ml Nitrogen at 17° and 719 mm pressure

calc. N 1.67% found N 1.53%

3. Octammine-μ-amido-μ-hydroxo dicobalt(III) sulfate

$$\left[(NH_3)_4Co\begin{matrix}\diagup NH_2 \diagdown\\ \diagdown OH \diagup\end{matrix}Co(NH_3)_4\right]\ (SO_4)_2 \cdot 2H_2O$$

0.3004 g gave 5.3 ml Nitrogen at 18° and 722 mm pressure

calc. N 1.81% found N 1.94%

When tested with alkaline pyragallol solution, the volume of remaining gas was unchanged; it consequently consisted of pure nitrogen.

B. Measurements with the sulfate of the green series

The picture of the decomposition process of the sulfate of the green series differs in that not only nitrogen, but also oxygen is formed. The oxygen is evolved from the action of the sulfuric acid with only gentle heating and, if one works carefully, oxygen alone is evolved up to the point when the salt completely dissolves to give a purple-violet solution. Nitrogen

is evolved only when the solution is heated more strongly. The amount of Nitrogen corresponds to the conversion of the trivalent cobalt into divalent; consequently the amount of oxygen corresponds to the conversion of the higher valence of cobalt into trivalent.

For example, the following results were obtained:

0.3149 g gave 4.8 ml Nitrogen and 11.10 ml Oxygen at 19° and 727 mm pressure, corresponding to 1.68% Nitrogen and 4.43% Oxygen.

Since the salt contains 22.2% Co, then for two cobalt atoms this results in:

$$N = \frac{1.68 \times 118}{22.2} = 8.93\% \text{ Nitrogen} = 2/3 \text{ atom}$$

calc. for 2/3 atom: N = 14.2 = 9.3%

$$O = \frac{4.43 \times 118}{22.2} = 24.4\% \text{ Oxygen} = 1\tfrac{1}{2} \text{ atoms}$$

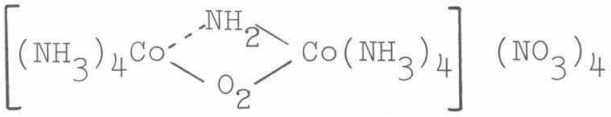
calc. for 3/2 atoms: O = 16 x 1.5 = 24% .

We therefore find that in the conversion of the higher [66]
valence of cobalt into trivalent the amount of oxygen corresponding to 3/2 atoms is bonded to each pair of cobalt atoms. Just how this great amount of oxygen is to be structurally incorporated into the formula is thoroughly discussed in the theoretical section. It must be assumed that a peroxide oxygen molecule is present which is bonded to one trivalent and one tetravalent cobalt atom.

In the conversion of the trivalent into the divalent cobalt, an amount of nitrogen corresponding to 1/3 atom bonded to each cobalt atom is released, as is to be expected.

If the heating in the operations described is not done carefully, less oxygen and more nitrogen will result. The total amount of the gas, however, if converted into oxygen equivalents, agrees with that required by theory, as the following experimental examples show:

> 0.3627 g gave 17.8 ml gas at 19° and 727 mm pressure of which 10.8 ml were Oxygen and 5.5 ml Nitrogen; this amounts to 1.69% Nitrogen and 4.25% Oxygen, which corresponds to 7.16% Oxygen.
>
> 0.2854 g gave 13.7 ml gas at 17° and 727 mm pressure; of which 4.8 ml were Nitrogen and 7.38 ml Oxygen; this amounts to 2.11% Nitrogen and 3.69% Oxygen, which corresponds to 7.30% Oxygen.
>
> calc: 7.5% Oxygen .

C. Nitrate: 

By working up Vortmann's Sulfate with nitric acid, green octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate is immediately obtained in a nearly pure condition. By recrystallization from warm, dilute aqueous nitric acid solution, the salt is further purified, and separates out in dark green prismatic crystals. It is very soluble in water, giving a neutral solution, and reprecipitates in the form of leek-green, cotton-like matted fine needles on the addition of nitric acid. Aqueous solutions

decompose very quickly, losing their green color and becoming first yellow and then brown as cobalt oxide precipitates. [67]

0.1557 g gave 0.0885 $CoSO_4$

0.1286 g gave 0.0734 $CoSO_4$

0.1617 g gave 49.7 ml Nitrogen at 17° and 708 mm pressure

0.1060 g gave 32.5 ml Nitrogen at 15° and 712 mm pressure

0.1495 g gave 0.0709 g H_2O

	calc. for $Co_2N_{13}O_{14}H_{26}$	found	
Co	21.4%	21.54%	21.63%
N	33.1	33.54	33.35
H	4.75	5.27	

That the nitrate is water-free is also confirmed by the fact that it does not lose any weight after being heated at 100° for long periods.

A hydrated nitrate has been described previously[1]; however,

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[1]Zeitschr. f. anorg. Chem. (1898) 16:134

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the existence of this compound has not been confirmed in our renewed investigation. The salt precipitated from a cold dilute solution of the nitrate by the addition of a little nitric acid consists of long leek-green needles which are, generally, water free, as is shown by the following analyses.

Sample I 0.1008 g gave 0.0572 g $CoSO_4$

0.1070 g gave 31.6 ml Nitrogen at 17° and 723 mm pressure

Sample II 0.1068 g gave 0.0600 g $CoSO_4$

0.1134 g gave 34.00 ml Nitrogen at 19° and 724 mm pressure

	calc.	found I	found II
Co	21.4%	21.57%	21.40%
N	33.1	33.55	33.39

D. Sulfate: $\left[(H_3N)_4Co\begin{smallmatrix}O_2\\NH_2\end{smallmatrix}Co(NH_3)_4\right](SO_4)_2 \cdot 2H_2O$

The sulfate is formed when aqueous solutions of the other salts are treated with dilute sulfuric acid. The precipitation [68] is quantitative since it is completely insoluble in water. The salt consists of small greenish-gray, silvery, plate-like prisms both ends of which look like swallowtails.

The sulfate dissolves in concentrated sulfuric acid to give a yellow-brown solution. The salt can be reprecipitated by greatly diluting the solution with water. It is converted into the chloride by triturating it with concentrated hydrochloric acid, and into the nitrate by trituration with concentrated nitric acid.

Sample I 0.0634 g gave 0.0375 g $CoSO_4$

0.1722 g gave 0.1020 g $CoSO_4$

0.1120 g gave 0.0995 g $BaSO_4$

0.1510 g gave 0.0790 g H_2O

Sample II 0.1482 g gave 0.0875 g $CoSO_4$

0.0785 g gave 16.7 ml Nitrogen at 20° and 718 mm pressure

Sample III 0.1291 g gave 0.0764 g $CoSO_4$

0.0757 g gave 16 ml Nitrogen at 16° and 718 mm pressure

0.1286 g gave 0.1151 g $BaSO_4$

0.1292 g gave 0.0683 g H_2O (combustion)

	calc. for $Co_2N_9S_2O_{10}H_{26} \cdot 2H_2O$	found			
			I	II	III
Co	22.22%	22.34%	22.45%	22.37%	22.52%
N	23.80	--	--	22.94	23.85
SO_4	36.20	36.51	--	--	36.89

E. <u>Chloride</u>: $\left[(H_3N)_4Co\begin{matrix}NH_2\\O_2\end{matrix}Co(NH_3)_4\right]Cl_4 \cdot 1H_2O$

The chloride is best prepared from the sulfate by triturating it two or three times with concentrated hydrochloric acid. The resulting chloride can be precipitated from the concentrated aqueous solution by adding concentrated hydrochloric acid, giving small green crystals that are then sucked dry and washed with alcohol and ether.

0.1542 g gave 0.1020 g $CoSO_4$ [69]

0.0790 g gave 0.0525 g $CoSO_4$

0.0934 g gave 0.0616 g $CoSO_4$

0.0608 g gave 15.0 ml Nitrogen at 17° and 724 mm pressure

0.0518 g gave 12.8 ml Nitrogen at 17° and 721 mm pressure

0.0484 g gave 12.0 ml Nitrogen at 17° and 720 mm pressure

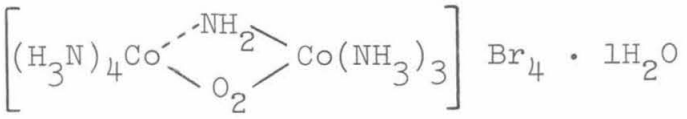
0.0600 g gave 0.0742 g AgCl

0.0464 g gave 0.0570 g AgCl

	calc.	found		
Co	25.50%	25.08%	25.19%	25.00%
N	27.30	27.13	27.22	27.21
Cl	30.60	30.58	30.38	

The chloride is very soluble in water. Dilute solutions decompose on standing and turn yellow-brown after a short time, but acidified solutions are stable for longer periods.

A one percent solution shows the following behavior: on addition of sodium sulfate, green prismatic crystals of the sulfate are formed; sodium phosphate yields a yellow-green precipitate of strongly intergrown microscopic crystals; potassium dichromate gives small star-like crystals. With platinum chloride a dark green precipitate of prismatic platelets with blunt end surfaces is formed; with potassium chloroplatinate, a yellowish precipitate of six-sided crystals results. Potassium ferrocyanide gives needle-like crystals, while no precipitate is formed with potassium ferricyanide. Potassium cyanide, potassium iodide and potassium gold chloride do not give any precipitates.

F. Bromide: 

The bromide is prepared from the sulfate in a way similar to that used for the chloride. It forms a dark green micro-crystalline powder that is very soluble in water.

The dark green color of the solution changes to yellow-brown after some time as the compound decomposes.

0.0410 g gave 0.1980 g $CoSO_4$ [70]

0.0980 g gave 0.1150 g AgBr

0.0480 g gave 8.7 ml Nitrogen at 17° and 717 mm pressure

	calc. for $Co_2N_9H_{26}O_2Br_4 \cdot 1H_2O$	found
Co	18.4%	18.3%
N	19.7	19.75
Br	49.9	49.8

G. Dithionate: $\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\O_2\end{smallmatrix}Co(NH_3)_4\right](S_2O_6)_2$

This salt is obtained by treating an aqueous solution of the nitrate containing some acetic acid with a concentrated solution of dithionate. It is composed of sparkling flaky crystals which appear brown because of their strongly colored surface. Its natural green color becomes apparent when a little concentrated hydrochloric acid is applied. It is nearly insoluble in water.

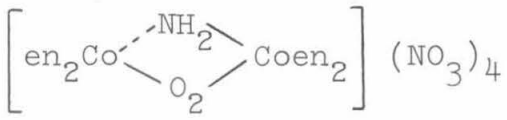
0.1145 g gave 0.0566 g $CoSO_4$

0.1180 g gave 0.0583 g $CoSO_4$

0.1210 g gave 22.3 ml Nitrogen at 21° and 735 mm pressure

	calc. for $Co_2N_9H_{26}S_4O_{14}$	found	
Co	18.97%	18.81%	18.80%
N	20.25	20.17	

IX. Tetraethylenediamine-μ-amido-μ-peroxo series

A. Nitrate: 

Four grams of octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate is stirred into a suspension in 60 ml of water, treated with 25 g of 10% aqueous ethylenediamine, and heated in a water bath until the ammonia odor disappears, which takes about 1 1/4 hours. The resultant brown solution is cooled and treated with nitric acid at room temperature until the color changes to olive-green. The solution is then cooled in an ice bath and after a short while, a slurry of crystals forms which is removed, sucked dry and washed with alcohol and ether. The crude product is dissolved in the minimum amount of cold water, [71] filtered, precipitated with HNO_3 and washed with alcohol and ether. Yield: about 3 g of green needles.

0.0786 g gave 0.0363 g $CoSO_4$

0.1120 g gave 0.0522 g $CoSO_4$

	calc. for $Co_2C_8N_{13}H_{34}O_{14}$	found	
Co	18.04%	17.97%	17.73%

When alcohol is added to the brown-green nitric acid mother liquor, a yellow salt precipitates in addition to some additional green salt. This is dissolved in a little water, precipitated with ammonium bromide, sucked dry, redissolved and reprecipitated from the aqueous solution with ammonium bromide.

0.0835 g gave 0.0234 g $CoSO_4$

0.1005 g gave 0.0282 g $CoSO_4$

	calc. for $[Coen_3]Br_3 \cdot 4H_2O$	found	
Co	10.70%	10.66%	10.67%

The secondary product is thus formed by the decomposition of the complex series and consists of a little triethylenediamine cobalt(III) salt. If a solution of the nitrate containing some acetic acid is treated with potassium thiocyanate or sodium iodide, a reduction occurs instantly and a brown thiocyanate, or a black periodide salt respectively, precipitates. These salts are derivatives of the tetraethylenediamine-μ-amido-μ-hydroxo dicobalt(III) series:

$$\left[en_2Co\begin{matrix}NH_2\\OH\end{matrix}Coen_2\right] X_4 \cdot$$

B. Bromide: $\left[en_2Co\begin{matrix}NH_2\\O_2\end{matrix}Coen_2\right] Br_4 \cdot 5H_2O$

The bromide, in the form of a dense, granular, crystalline crust, is very quickly formed when a cold saturated solution of the nitrate is treated with ammonium bromide. The light transmitted through the crystals is yellow green, while with reflected light they appear almost black. The salt can be purified by reprecipitation from an aqueous solution by use of ammonium bromide.

The green bromide can also be obtained from the olive green [72] mother liquor of the red bromide preparation described in the next section. If this solution is allowed to stand for a short

time, the green bromide precipitates in copious amounts.

The salt is very soluble in water, giving a yellow-green neutral solution.

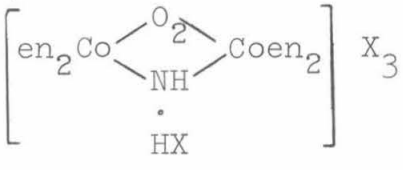
0.1445 g gave 0.0548 g $CoSO_4$

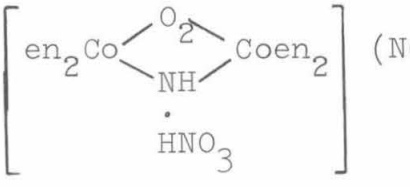
0.1543 g gave 0.1396 g AgBr

	calc. for $Co_2C_8N_9H_{34}O_2Br_4 \cdot 5H_2O$	found
Co	14.46%	14.43%
Br	39.19	38.49

Other bromides containing fewer than five water molecules appear to exist. We are presently carrying out a thorough investigation of this series.

X. Tetraethylenediamine-μ-ammonium-μ-peroxo dicobalt(III) salts†



A. Nitrate: 

Twenty-five grams of 10% aqueous ethylenediamine are added to an aqueous suspension of ~ 4 g of octammine-μ-amido-μ-peroxo nitrate and the solution is heated until the ammonia odor disappears. After the brown solution has been well cooled, nitric acid is added dropwise with constant stirring until the

color has changed to blood-red. The solution is then placed in a freezing mixture. A bright red crystalline powder soon separates out which is removed and washed with alcohol and ether. If the red salt is allowed to stand in the solution too long, it is transformed into the green form. Yield: $3\frac{1}{2}$ grams.

0.1558 g gave 0.0701 g $CoSO_4$ [73]

0.0461 g gave 0.0208 g $CoSO_4$

0.1684 g gave 40.72 ml Nitrogen at 19° and 722 mm pressure

	calc. for $Co_2C_8N_{13}H_{34}O_{14} \cdot 2H_2O$	found	
Co	17.10%	17.12%	17.17%
N	26.37	26.26	

B. Bromide: $\left[en_2Co\begin{matrix}O_2\\NH\end{matrix}Coen_2\right]Br_3 \cdot 3H_2O$ †

HBr

Twelve grams KBr are added to a solution of 4 g of the red nitrate in 80 ml of water, quickly yielding a precipitate of red crystals. These are filtered off after three to four minutes and washed with alcohol and ether. The mother liquor has an olive green color. Yield: 2 grams.

0.1415 g gave 0.0566 $CoSO_4$

0.1533 g gave 0.1475 AgBr

0.0885 g gave 0.0051 H_2O (at 100-105°)

	calc. for $Co_2C_8N_9H_{34}O_2Br_4 \cdot 3H_2O$	found
Co	15.12%	15.23%
Br	41.00	40.95
H_2O	6.92	5.76

The red bromide dissolves in water, giving a brown solution; this solution is acidic because of hydrolysis. On the addition of mineral acids, the solution turns first red and then almost immediately green.

The bromide can be obtained with a different water content (monohydrate) in the following way. A mixture of 4 g of red and green bromide, such as that often precipitated on the neutralization of the above solutions, is stirred with 5 ml of ammonia and is triturated with 5 g of NaI. The precipitated salt is filtered out and washed with alcohol and ether. This salt is then ground with 6 g of AgCl in 20 ml of water and hydrochloric acid is added dropwise to the filtered solution until the color changes to red. On the addition of ammonium bromide to this solution, red bromide quickly precipitates; this is removed, again reprecipitated, and finally washed with alcohol and ether.

0.0933 g gave 0.0390 $CoSO_4$ [74]
0.1497 g gave 0.1517 AgBr
0.0712 g gave 0.0018 H_2O (at 100-105°)

	calc. for $Co_2C_8N_9H_{34}O_2Br_4 \cdot 1H_2O$	found
Co	15.85	15.91
Br	42.48	43.12
H_2O	2.41	2.52

This salt can be obtained much more quickly by dissolving the brown iodide with the stoichiometric amount of $AgNO_3$ in a little water, shaking it thoroughly, acidifying the filtered solution with the minimum amount of HCl and then precipitating the salt with ammonium bromide. The red bromide thus obtained must be filtered off and washed with alcohol very quickly, because it converts into the green isomer particularly easily.

0.1152 g gave 0.0487 g $CoSO_4$

0.1602 g gave 0.1607 g AgBr

	calc. for $Co_2C_8N_9H_{34}O_2Br_4 \cdot 1H_2O$	found
Co	15.85%	16.08%
Br	42.98	42.69

XI. Tetraethylenediamine-μ-imido-μ-peroxo dicobalt(III,IV) iodide

Eight ml of ammonia are added to a paste of 4 g of tetraethylene diamine-μ-amido-μ-peroxo dicobalt(III,IV) bromide and 15 ml water, and 10 g of NaI are ground with the resulting mixture, giving a thick black-brown paste. About 1½ g of thiosulfate are now added and ground with the paste. The solid is then separated, sucked dry and washed with alcohol. This crude product is dissolved in 40 ml of water, filtered and 40 g of KI are added to the solution to precipitate the salt. The latter, consisting of small brown needles, is pure after a second such reprecipitation. Yield: 38 grams.

0.1591 g gave 0.0566 g $CoSO_4$

0.1488 g gave 0.1187 g AgI

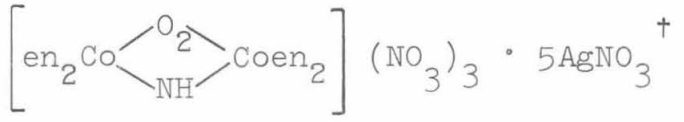
	calc. for $Co_2C_8N_9H_{33}O_2I_3 \cdot 5H_2O$	found	[75]
Co	13.47%	13.53%	
I	43.49	43.07	

The same iodide is obtained as an intermediate in the reduction of μ-peroxo nitrate with sodium iodide in acetic acid solution.

The aqueous solution of the iodide does not give a precipitate when KBr or NH_4Br is added. Small brown needles of the nitrate can be precipitated from a solution of the iodide by triturating it with the stoichiometric amount of $AgNO_3$, filtering off the resulting AgI and allowing the solution to stand in a desiccator over H_2SO_4. By shaking the iodide with AgCl a solution of the chloride can be obtained which, however, does not yield any crystals upon concentration of the solution. K_2PtCl_4 gives dark red-brown platinum(II) chloride adduct, and $KAuCl_4$ gives the dark chamois red gold(III) chloride adduct.

If some hydrochloric acid is added to a solution of the chloride, the solution first turns red then, after a little while, green; while if nitric acid is added instead the solution turns green almost immediately. The red bromide can be precipitated from a solution of the chloride by the addition of hydrobromic acid and ammonium bromide.

Adduct of the Nitrate and Silver Nitrate



3.8 g of tetraethylenediamine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate are made into a paste with 5 ml of water and ground with 8 ml of ammonia and 8 g NaI while some thiosulfate is added. The precipitated salt is removed, washed with alcohol and ether and reprecipitated from aqueous solution with KI. Yield: 2.8 grams. This is dissolved in 18 ml of water and ground with 1.8 g of $AgNO_3$. The resulting solution is filtered, 3 more g of $AgNO_3$ is added and the solution placed in an ice bath. A beautifully crustallized, dark brown salt soon precipitates out which, as a rule, generally contains some reduced silver. In order to purify it, it is dissolved in a little water and reprecipitated by addition of $AgNO_3$. Yield: about 3 grams.

0.1499 g gave 0.0406 AgCl [76]

0.1492 g gave 0.0520 $CoSO_4$

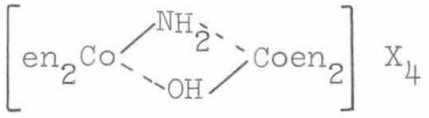
0.1371 g gave 27.90 ml Nitrogen at 15° and 722 mm pressure

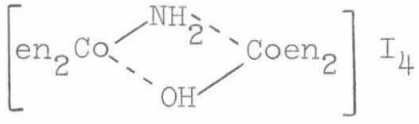
0.1319 g gave 26.71 ml Nitrogen at 14.5° and 720 mm pressure

	calc. for $Co_6C_{24}N_{36}H_{99}O_{33} \cdot 5AgNO_3$	found	
Co	13.52%	13.26%	
Ag	20.43	20.38	
N	21.93	22.71	22.52

Similar addition compounds may also be prepared with other metal salts. With $Cu(NO_3)_2$ an apple green crystalline powder is obtained, and with $HgCl_2$ shining red crystals can be precipitated from dilute solutions.

XII. Tetraethylenediamine-μ-amido-μ-hydroxo dicobalt(III) salts



A. Iodide: 

Six grams of NaI are added to a suspension of 4 g of green tetraethylenediamine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate in 30 ml of water to which had been added 3-4 ml of acetic acid. A thick black slurry of a periodide forms immediately. An excess of thiosulfate is added and the mixture warmed until a dark red solution results. On cooling, most of the iodide precipitates out; it is removed, sucked dry and washed with alcohol and ether. More iodide can be recovered from the mother liquor by adding more sodium iodide. Yield of light red crystalline powder: 3 grams.

0.1538 g gave 0.0534 g $CoSO_4$
0.1135 g gave 0.1169 g AgI

	calc. for $Co_2C_8N_9H_{35}OI_4$	found
Co	13.14%	13.21%
I	56.48	55.67

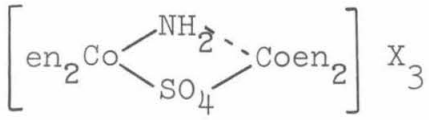
B. Bromide: $\left[en_2Co\begin{smallmatrix}NH_2\\OH\end{smallmatrix}Coen_2\right]Br_4 \cdot 4H_2O$

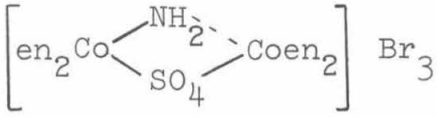
2.5 g glacial acetic acid and 3 g KI in 5 ml of water are [77]
added to 3 g of tetraethylenediamine-μ-amido-μ-peroxo nitrate that has been made into a paste with 15 ml of water and the mixture is well stirred, yielding a thick slurry of black periodide. 1½ to 2 g of thiosulfate is added and the mixture stirred until the precipitate has taken on a pale red color. The precipitate is filtered off, mixed three times with about 5 g of ammonium bromide and a little water, each time removing the precipitate, dissolving it in the minimum amount of water, and reprecipitating it with ammonium bromide. The bromide thus prepared consists of small, shiny, dark red crystals. A considerable amount of bromide can also be precipitated from the first iodide liquor by using ammonium bromide. Yield: 2 grams.

0.1253 g gave 0.0577 g $CoSO_4$
0.1808 g gave 0.1995 g AgBr

	calc. for $Co_2C_8N_9H_{35}OBr_4 \cdot 4H_2O$	found
Co	17.37	17.53
Br	47.10	46.97

XIII. Tetraethylenediamine-μ-amido-μ-sulfato dicobalt(III) salts*



Bromide: 

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*Translator's note: The heading for this section reads: "Sulfato-tetraethylenediamine-μ-amido-μ-hydroxo dicobalt(III) salts." I have here assumed that the "μ-hydroxo" was in error as both the diagrams and the analysis results do not include a hydroxo bridge. The whole situation is made more confusing by the lack of any mention in this section as to where the sulfato bridge comes from; it is not in the starting material and is nowhere introduced as a reagent.

Four grams of tetraethylenediamine-μ-amido-μ-peroxo nitrate are made into a paste in 20 ml of water and to it are added 4 ml of glacial acetic acid and an excess of potassium thiocyanate. A brown thiocyanate separates out and can be redissolved by warming the mixture to 55° in a water bath. Red crystals are formed on cooling. One gram of this salt is added to 4 ml of concentrated HNO_3 in small portions since a vigorous reaction ensues. The reaction mixture is allowed to stand, with occasional stirring, until no more nitrous oxides are liberated. The solution is then well cooled and mixed with alcohol, the

precipitate sucked dry, dissolved in a little water and the resulting solution treated with ammonium bromide. After some time a red crystalline powder precipitates which consists of tetraethylenediamine-μ-amido-μ-sulfato dicobalt(III) bromide. [78]

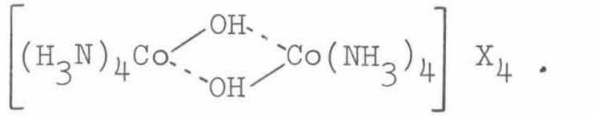
0.1016 g gave 0.0442 g $CoSO_4$

0.1370 g gave 0.1075 g AgBr

0.2455 g gave 0.0605 g $BaSO_4$

	calc. for $Co_2C_8N_9H_{34}SO_4Br_3$	found
Co	16.62%	16.55%
Br	33.80	33.39
S	4.51	3.96

XIV. Octammine-di-μ-hydroxo dicobalt(III) salts



I have already reported the preparation of the starting material of this series, the constitutional determination, and the properties of a few of its salts (chloride, bromide, nitrate, thiosulfate, dithionate, and sulfate).[1] In order to thoroughly

[1] Ber. d. d. Chem. Ges. (1907) 40:4434

characterize this series, Mr. E. Kindscher[2] has investigated a

[2] The Basic Metal Salts from the Standpoint of the Theory of the Hydroxyl Salts. Inaugural Dissertation, Zurich, 1909.

number of these salts, which are described below. These salts were all derived from the chloride, which was prepared according to the methods reported earlier.

A. Iodide: $\left[(NH_3)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right] I_4 \cdot 2H_2O$

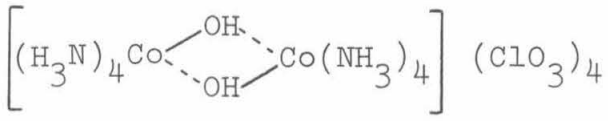
The iodide is synthesized by treating a solution of 2 g of di-μ-hydroxo chloride in 15 ml of water with solid potassium iodide.[1]

[1] Ber. d. d. chem. Ges. (1907) 40:4438

It is advantageous not to use too large an amount of chloride solution and to add only as much potassium iodide as is necessary to start the precipitation, since otherwise the salt decomposes very easily, giving a brown color. A beautifully crystallized [79] dark violet salt with only a touch of brown color is thus obtained. The precipitate is filtered off quickly as possible and washed with alcohol and ether. The dried salt is very soluble in water and, as a solid, decomposes above 60°. It turns brown on standing in the air for a long time.

0.1050 g gave 0.0397 g $CoSO_4$
0.1011 g gave 0.0378 g $CoSO_4$
0.1114 g gave 0.1253 g AgI
0.1276 g gave 0.0053 g H_2O

	calc. for $Co_2N_8H_{26}O_2I_4 \cdot 2H_2O$	found	
Co	14.17%	14.29%	14.14%
I	61.01	60.77	
H_2O	4.33	4.15	

B. Chlorate: 

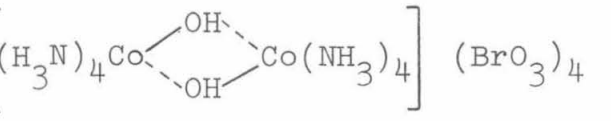
Solid sodium chlorate is added to a saturated solution of di-μ-hydroxo chloride. On standing, small crystals of a bright red salt separate out of the solution. These are filtered out, washed with alcohol and ether and dried. It is very soluble in water and explosive when heated.

0.1025 g gave 0.0512 g $CoSO_4$

0.1008 g gave 0.0505 g $CoSO_4$

0.2016 g gave 0.1865 g AgCl

	calc. for $Co_2N_8H_{26}Cl_4O_{14}$	found	
Co	18.96%	19.02%	19.05%
Cl	22.78	22.87	

C. Bromate: 

Two g of di-μ-hydroxo chloride are dissolved in 15 ml of water and solid sodium bromate is added. After a while a well crystallized ruby-red salt precipitates out which is sucked dry, washed with alcohol and ether and dried. It is very soluble in water.

0.1136 g gave 0.0432 g $CoSO_4$ [80]

0.1014 g gave 0.0390 g $CoSO_4$

0.1514 g gave 0.1416 g AgBr

	calc. for $Co_2N_8H_{26}Br_4O_{14}$	found	
Co	14.74%	14.44%	14.60%
Br	39.96	39.83	

D. Iodate: $\left[(H_3N)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right](IO_3)_4$

A dilute solution of the di-μ-hydroxo chloride is treated with a solution of sodium iodate. After standing for a while a bright violet, beautifully crystallized salt is formed which is insoluble in water. It is filtered out, washed with water, alcohol and ether and dried.

0.1026 g gave 0.0321 g $CoSO_4$
0.1175 g gave 0.0368 g $CoSO_4$
0.1214 g gave 0.1141 g AgI
0.1066 g gave 0.1011 g AgI

	calc. for $Co_2N_8H_{26}I_4O_{14}$	found	
Co	11.94%	11.89%	11.91%
I	51.38	50.82	51.22

E. Oxalate: $\left[(H_3N)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right](C_2O_4)_2 \cdot 2H_2O$

A solution of arbitrary concentration of di-μ-hydroxo chloride is prepared and solid sodium oxalate is added to it. On standing undisturbed, fine, ruby-red crystals of oxalate separate out. These are filtered out, washed with ether and

alcohol and dried. The salt is insoluble in water and does not lose any water of hydration at 80°.

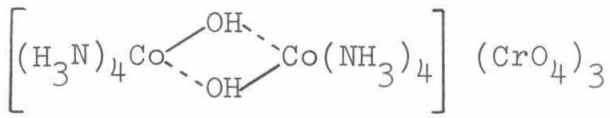
0.1053 g gave 0.0660 g $CoSO_4$

0.1008 g gave 0.0630 g $CoSO_4$

0.1250 g gave 26.10 ml Nitrogen at 20° and 723 mm pressure

0.1124 g gave 0.0608 g H_2O and 0.0389 g CO_2

	calc. for $Co_2N_8C_2H_{26}O_{10}$	found	
Co	23.57%	23.83%	23.81%
N	22.44	22.69	
C	9.59	9.44	
H	6.05	6.02	

F. Chromate:  [81]

A dilute solution of di-μ-hydroxo chloride is treated with solid sodium chromate. The light brown di-μ-hydroxo chromate, which is completely insoluble in water, immediately precipitates out. The wet salt has a silky luster, but when dry it appears earthy. All attempts to crystallize it were unsuccessful. For the analysis the salt was washed with water, alcohol and ether and dried.

0.2038 g gave 0.0603 g Cr_2O_3

0.2038 g gave 0.1197 g $CoSO_4$

	calc. for $Co_2N_8H_{26}O_{10}Cr_2$	found
Cr	20.01%	20.26%
Co	22.66	22.33

G. Phosphate: $\left[(H_3N)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right](HPO_4)_2 \cdot 6H_2O$

A dilute solution of di-μ-hydroxo chloride was treated with solid sodium phosphate, immediately giving the completely insoluble di-μ-hydroxo phosphate in fine rose-red lustrous crystallites. The salt was filtered off, washed with water, alcohol and ether and dried.

0.2015 g gave 0.1049 g $CoSO_4$
0.2041 g gave 0.1051 g $CoSO_4$
0.2015 g gave 0.0756 g $Mg_2P_2O_7$
0.2041 g gave 0.0793 g $Mg_2P_2O_7$
0.1454 g gave 0.0265 g H_2O

	calc. for $Co_2N_8H_{28}O_{10}P_2 \cdot 6H_2O$	found	
Co	20.04%	19.80%	19.60%
P	10.53	10.42	10.83
H_2O	18.37	18.23	

H. Chloroplatonate: $\left[(H_3N)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right](PtCl_4)_2$

A dilute solution of di-μ-hydroxo chloride was treated with solid potassium chloroplatonate, giving small crystals of a brick-red, insoluble salt. This was filtered out, washed with alcohol and ether and dried. [82]

0.1580 g gave 0.1150 g $CoSO_4$ + Pt

of which 0.0644 g Pt remained when the $CoSO_4$ was washed out.

	calc. for $Co_2N_8H_{26}O_2Pt_2Cl_8$	found
$CoSO_4$ + Pt	0.1149 g	0.1150 g
Pt	40.50%	40.76%

I. <u>Chloroplatinate</u>: $\left[(H_3N)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right](PtCl_6)_2 \cdot 6H_2O$

Two grams of di-μ-hydroxo chloride are dissolved in 25 ml of water and treated with a very dilute solution of chloroplatinic acid. A copper red salt precipitates out some time afterwards as well-formed, lustrous, needle-like crystals. It is insoluble in water. After being filtered off, it is washed with water, alcohol and ether and then dried.

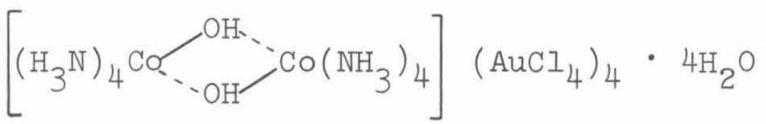
0.1098 g gave 0.0098 H_2O

0.1003 g gave 0.0571 $CoSO_4$ + Pt

Of this, 0.0318 g Pt remained after the $CoSO_4$ was washed out.

	calc. for $Co_2N_8H_{26}O_2Pt_2Cl_{12} \cdot 6H_2O$	found
H_2O	8.92%	8.92%
$CoSO_4$ + Pt	0.0573 g	0.0571 g
Pt	0.0322 g	0.0318 g

J. Gold(III) chloride adduct:

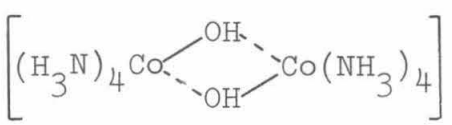


A solution of 2 g of di-μ-hydroxo chloride dissolved in 25 ml of water is treated with a concentrated solution of potassium gold chloride. On standing undisturbed a brick red precipitate forms which is composed of very small crystals. This compound is barely soluble in water.

0.1102 g gave 0.0046 g H_2O

0.2006 g gave 0.0923 g Au

	calc. for $Co_2N_8H_{26}O_2Au_4Cl_{16} \cdot 4H_2O$	found
H_2O	4.20%	4.17%
Au	45.95	46.01

K. Fluorosilicate:  [83]

A solution of sodium fluorosilicate is added to a solution of 2 g of di-μ-hydroxo chloride in 30 ml of water. After standing for a while, a lustrous, bright violet precipitate settles out which is washed with water, alcohol and ether and dried. This salt is insoluble in water.

0.1225 g gave 0.0660 g $CoSO_4$

0.1199 g gave 0.0645 g $CoSO_4$

	calc. for $Co_2N_8H_{26}O_2Si_2F_{12}$	found	
Co	20.58%	20.49%	20.43%

XV. Tetraethylenediamine-di-μ-hydroxo dicobalt(III) salts

$$\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right] X_4 \cdot$$

This series has been investigated by Mr. J. Rapiport.[1] The

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[1] Jos. Rapiport, On carbonate salts of the diethylenediamine cobalt series. Inaugural Disertation. Zurich 1909.

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starting material used in the preparation of the salts of this series is cis hydroxoaquodiethylenediamine cobalt(III) dithionate, $\left[\begin{matrix}HO\\H_2O\end{matrix}Coen_2\right] S_2O_6$, which has been described earlier.[2] A better

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[2] Ber. d. d. Chem. Ges. (1907) 40:284

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method, giving much more reproducible results, has been devised for the preparation of this starting material.

A. Preparation of cis hydroxoaquodiethylenediamine cobalt(III) dithionate

One begins with the very easily prepared hexaethylenediamine-

hexa-μ-hydroxo tetracobalt(III) nitrate,[3]

---

[3]Ber. d. d. chem. Ges. (1907) 40:2121

$$\left[Co \begin{pmatrix} OH \\ OH \end{pmatrix} Coen_2 \right]_3 (NO_3)_6 ,$$

3 g of which are mixed with 3 ml of saturated hydrochloric acid [84]
at 0°. The hexa-μ-hydroxo nitrate dissolves with the evolution of chlorine, giving a solution that is at first deep green but which slowly changes to violet and then to red. A drop of water is added as soon as all of the salt has gone into solution, whereupon the color changes to ruby red. Beautiful ruby-red crystals of cis diaquodiethylenediamine cobalt(III) chloride, $[(H_2O)_2\ Coen_2]\ Cl_3$, very soon precipitate out of the solution. This salt is filtered out and washed free of acid with alcohol. (Yield: 2 grams)

The conversion of this salt into hydroxoaquodiethylenediamine cobalt dithionate is handled in the following way. Five g of cis diaquo chloride are dissolved in 12 ml of water. To this solution 25 ml of pyridine are next added, and it is then mixed with 25 ml of cold saturated sodium dithionate solution. Light red-violet crystals of the hydroxo aquo dithionate are coaxed out of solution by scratching the side of the flask with a glass rod. This salt is then sucked dry, washed with water and alcohol and dried with ether. Yield: 4.5 grams.

B. Preparation of Tetraethylenediamine-di-μ-hydroxo dicobalt(III) dithionate

By drying hydroxoaquodiethylenediamine cobalt(III) dithionate to constant weight at 100°-110°, it is converted into tetraethylene-diamine-di-μ-hydroxo dicobalt(III) dithionate.

1.9007 g lost 0.0924 g H_2O at 110°

	calculated	found
H_2O	4.82%	5.26%

This process is represented by the equation:

$$O_6S_2\left[en_2Co\begin{matrix}OH\\OH_2\end{matrix}\right]+\left[\begin{matrix}H_2O\\HO\end{matrix}Coen_2\right]S_2O_6 =$$

$$2H_2O + O_6S_2\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right]S_2O_6$$

which corresponds exactly to that of the conversion of hydroxo-aquotetrammine cobalt(III) sulfate into octammine-di-μ-hydroxo dicobalt(III) sulfate.[1]

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[1] Ber. d. d. Chem. Ges. (1907) 40:4434

C. Tetraethylenediamine-di-μ-hydroxo dicobalt(III) bromide: [85]

$$\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right]Br_4 \cdot 4H_2O$$

Five g of tetraethylenediamine-di-μ-hydroxo dicobalt(III) dithionate and 10 g of ammonium bromide are mixed in 25 ml of water. After about 10 minutes the mixture is suction filtered. Since the product contains quite a bit of ammonium bromide, 10 ml of water is added and the mixture stirred to dissolve it. The residue is again suction filtered and redissolved in water. The salt appears to be quite soluble. The bromide is precipitated from this solution in the form of red-violet needles by addition of ammonium bromide. It crystallizes with 4 molecules of water of hydration, of which two are given up on drying at 100° or on standing over concentrated sulfuric acid in a desiccator.

0.1170 g gave 0.0452 g $CoSO_4$

0.0938 g gave 0.0360 g $CoSO_4$

0.1293 g gave 0.1254 g AgBr

0.1154 g gave 0.1108 g AgBr

0.1578 g gave 20.26 ml Nitrogen at 23° and 731 mm pressure

0.1632 g gave 21.00 ml Nitrogen at 22° and 733 mm pressure

	calc. for $Co_2N_8H_{34}O_2Br_4 \cdot 4H_2O$	found	
Co	15.05%	14.7 %	14.61%
N	14.28	14.26	14.36
Br	40.81	41.27	40.85

Analysis of the salt containing 2 waters of hydration:

0.1400 g gave 0.0567 g $CoSO_4$

0.1396 g gave 18.9 ml Nitrogen at 18° and 720 mm pressure

0.1373 g gave 0.1380 g AgBr

	calc. for $Co_2C_8N_8H_{34}O_2Br_4 \cdot 2H_2O$	found
Co	15.76%	15.40%
N	14.98	15.01
Br	42.76	42.77

The bromide is very soluble in water, giving a neutral, blue-red solution.

D. Cleavage of the bromide with concentrated hydrobromic acid

Five g of di-μ-hydroxo bromide were stirred with 10 ml of saturated (at 12°) hydrobromic acid solution while being strongly cooled. The reaction product was immediately placed on a clay plat and washed free of acid with alcohol. The salt thus prepared consists of pure cis dibromodiethylenediamine cobalt(III) bromide: $[Br_2Coen_2]Br$. [86]

0.0800 g gave 0.0286 g $CoSO_4$

0.1184 g gave 0.0425 g $CoSO_4$

0.0860 g gave 0.1156 g AgBr

	calc. for $CoN_4C_4H_{16}Br_3$	found	
Co	14.08%	13.61%	13.66%
Br	57.28	57.20	

E. Thiocyanate: $\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right](SCN)_4 \cdot 3H_2O$

If a solution of the bromide is treated with potassium thiocyanate, di-μ-hydroxo thiocyanate immediately precipitates

in the form of small purple crystals. Red-violet crystals can be obtained by recrystallization from a very dilute aqueous solution.

0.0904 g gave 0.0422 g $CoSO_4$

0.1232 g gave 0.0577 g $CoSO_4$

0.1384 g gave 31.4 ml Nitrogen at 20° and 718 mm pressure

0.1258 g gave 30.60 ml Nitrogen at 20° and 716 mm pressure

0.2130 g gave 0.2896 $BaSO_4$

	calc. for $Co_2C_{12}N_{12}S_4H_{34} \cdot 3H_2O$	found	
Co	17.41%	17.77%	17.83%
N	24.78	24.97	24.92
S	18.88	18.67	

F. Nitrate: $\left[en_2Co\begin{matrix}OH\\OH\end{matrix}Coen_2\right](NO_3)_4$

If sodium nitrate is added to a saturated solution of the bromide, the nitrate precipitates as a purple-colored powder. This can be recrystallized from water and obtained in the form of massive purple crystals. The salt contains no water of crystallization. It is fairly soluble in water, giving a blue-red solution.

0.1112 g gave 0.0540 g $CoSO_4$ [87]

0.1259 g gave 0.0624 g $CoSO_4$

0.1110 g gave 26.3 ml Nitrogen at 20° and 723 mm pressure

	calc. for $Co_4C_8N_{12}O_{14}H_{34}$	found	
Co	18.44%	18.48%	18.94%
N	26.25	26.26	

XVI. Octammine-di-μ-amido dicobalt(III) salts

Bromide: $\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}Co(NH_3)_4\right]Br_4 \cdot 4H_2O$.

Occasionally the product obtained in a preparation of cis dichlorotetrammine cobalt(III) chloride (Violeo chloride) from 150 g of octammine-di-μ-hydroxo dicobalt chloride was stored on a clay plate over phosphorus pentoxide. After about two days, the salt was observed to have partially changed in color to rusty brown. All of the Violeo chloride was dissolved in a minimum of water and some trans-dichloro salt (Praseo chloride) was filtered from the solution. The solution was then allowed to stand for about 1/2 hour, after which sodium dithionate was added. Beautiful, shiny, bright orange-yellow platelets separated out. This salt is almost insoluble in water. An equivalent amount of ammonium bromide and a little water were added and the mixture was stirred well. To remove excess ammonium bromide, the reaction product was removed, again triturated with a little water and finally filtered. By means of these operations the dithionate was converted to the bromide which when free of ammonium bromide is quite soluble in water. The salt was redissolved in water and reprecipitated by addition of ammonium bromide, giving an almost quantitative yield of micaceous, brick-red plates.

The purified salt, once filtered off and washed with alcohol and ether, gave the following analytical results:

0.1578 g gave 29.7 ml Nitrogen at 21° and 719 mm pressure [88]

0.1097 g gave 0.0503 g $CoSO_4$

0.1197 g gave 0.1331 g AgBr

0.2776 g lost 0.0311 g at 95°; it was slightly decomposed, however,

	calc. for $Co_2N_{10}H_{28}Br_4 \cdot 4H_2O$	found
Co	17.42%	17.45%
N	20.65	20.67
Br	47.20	47.32
H_2O	10.60	11.33

XVII. Preparation of Melanochloride

The grey salt mixture designated as Melanochloride serves as the starting material in the preparation of numerous salts which are described below. It is therefore desirable to have a somewhat more exact description of the preparation of this starting material.

One preparation method has already been reported.[1] The

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[1] Zeitschr. f. anorg. Chem. (1898) 16:159

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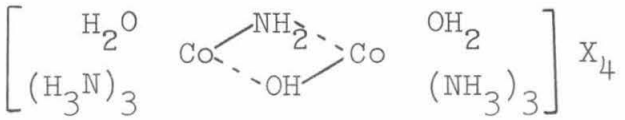
following one, worked out by J. Fürstenberg, is substantially faster.

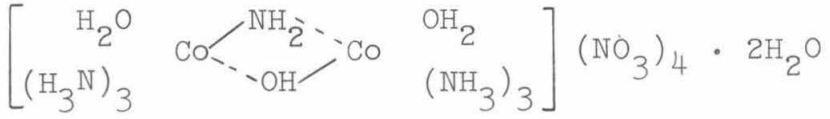
650 g of cobalt chloride, $CoCl_2 \cdot 6H_2O$, are dissolved in 400 ml of hot water and mixed with 2 liters of concentrated (25%)

ammonia. This mixture is heated to boiling and the precipitated cobalt oxide filtered off immediately from the resulting brown-yellow solution which is then allowed to stand in the free air for 48 hours. During this period the solution's color changes to brownish-red. A hard red crystalline crust is filtered out and the solution is then mixed with 3 liters of crude hydrochloric acid. The color changes to violet and a brown-red mixture of salts precipitates out and is removed as quickly as possible by suction filtration. This salt mixture is washed with cold water until it has a pure grey color and the wash water is brownish-violet. About 60 g of Melanochloride are obtained from 1 kg of cobalt chloride.

XVIII. Diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) salts [89]

By J. Fürstenberg



Nitrate: 

This salt is the starting material for a great number of the compounds described below and is identical to the salt which Fr. Steinitzer and I have previously described and assigned the following constitutional formula:[1]

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[1]Zeitschr. f. anorg. Chem. (1898) 16:161

$$\left[\begin{matrix}(H_2O)_2 \\ (H_3N)_3\end{matrix}\ \text{Co—NH—Co}\ \begin{matrix}(OH_2)_2 \\ (NH_3)_3\end{matrix}\right](NO_3)_4 .$$

The summary of the analyses shows that the values found earlier agree very well with a new constitutional formula now known to be correct.

To prepare the nitrate one begins with the Melanochloride, whose method of preparation has just been described. Twenty grams of finely pulverized Melanochloride are mixed in a roomy porcelain dish with a weakly acidified (HNO_3) solution of 36 g of $AgNO_3$ in 60 ml of water. The mixture is heated at 50° for a while. The silver chloride is filtered off from the deep brown liquid, which will be used primarily for the preparation of the hexammine-μ-amido-μ-hydroxo dicobalt(III) salts. This is solution A.

The silver chloride precipitate is repeatedly heated at 80° with 60 ml aliquots of weak aqueous nitric acid solution until it is colorless. The red aqueous extractions are combined and designated as solution B.

A few granules of ammonium nitrate are added to solution A, which is then allowed to stand for about 1/4 hour. After this time the red nitrate in the solution has completely precipitated; [90] it is then filtered out. The brown mother liquor is treated with concentrated hydrochloric acid and heated to 40°, yielding a precipitate of brown-black salt which serves as the starting material in the preparation of the hexammine-μ-amido-μ-hydroxo-μ-peroxo dicobalt(III,IV) salts.

For the isolation of the nitrate from solution B, ordinary alcohol is added until the solution is weakly turbid and it is then placed in a bath of freezing mixture. After a few hours, most of the nitrate has precipitated out in the form of small red crystals. The precipitation is repeated by the addition of more alcohol in order to recover the remaining nitrate from the solution.

To obtain the pure salt, the crude nitrate is dissolved with heating in a five-fold amount of water and after being cooled it is treated with concentrated HNO_3 until further addition does not yield any more precipitate.

Lustrous, bright red, platelike crystals are obtained by this process. The yield from a kilogram of cobalt chloride is about 15 g. On recrystallization from very dilute aqueous nitric acid solution the salt forms granite-red, flat, tetragonal prisms. The salt is much more soluble in warm solution than in cold, and forms acidic solutions in water.

Analyses: I. by Fr. Steinitzer

0.0500 g gave 0.02685 g $CoSO_4$

0.0500 g gave 12.0 ml Nitrogen at 13° and 726 mm pressure

0.0500 g gave 12.2 ml Nitrogen at 12° and 711 mm pressure

0.0500 g gave 0.0256 g H_2O

II. by J. Fürstenberg

0.1010 g gave 0.0548 g $CoSO_4$

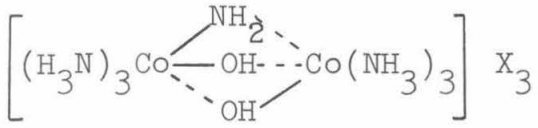
0.0909 g gave 0.0494 g $CoSO_4$

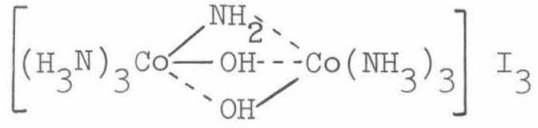
0.1027 g gave 26.1 ml Nitrogen at 22° and 715 mm pressure

0.0984 g gave 26.4 ml Nitrogen at 21° and 728 mm pressure

	calc. for $Co_2N_{11}O_{15}H_{25} \cdot 2H_2O$	I		II	
Co	20.60%	20.38%	20.38%	20.65%	20.60%
N	26.95	27.04	27.00	27.20	27.23
H	5.21	5.12	5.12	--	

XIX. Hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts [91]



A. Iodide: 

This salt results when solid potassium iodide is added to a dilute solution of diaquo hexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate. If a too concentrated solution is used, the nitrate will be co-precipitated with the iodide. The recrystallization of the iodide is difficult, as it is easily decomposed by heating.

The iodide consists of brownish-red fine needles that are only slightly soluble in cold water. Iodine is liberated when the salt is heated in aqueous solution.

0.1135 g gave 0.0541 g $CoSO_4$

0.1159 g gave 0.0557 g $CoSO_4$

0.1075 g gave 0.1157 g AgI

0.1018 g gave 0.1100 g AgI

	calc. for $Co_2N_7O_2H_{22}I_3$	found	
Co	18.10%	18.15%	18.29%
I	58.40	58.20	58.41

The salt gives a neutral solution when dissolved in water.

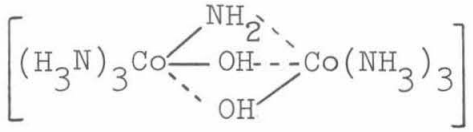
B. Bromide: $\left[(H_3N)_3Co\begin{matrix}\diagup NH_2 \diagdown \\ -OH\text{---}Co(NH_3)_3 \\ \diagdown OH \diagup\end{matrix}\right] Br_3 \cdot 1H_2O$

The bromide is obtained if a warm half-saturated solution of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate is saturated with ammonium bromide. The salt precipitates as fine, dark red needles from the cooled solution.

The bromide can also be prepared from the iodide. One gram of iodide is pulverized with 2 g of well washed silver bromide; the resulting silver iodide is filtered off and absolute alcohol is added to the solution until it remains turbid. On standing, the bromide precipitates as small needles. The bromide is fairly difficult to dissolve; aqueous solutions are neutral.

0.1042 g gave 0.0612 g $CoSO_4$ [92]
0.1049 g gave 0.0614 g $CoSO_4$
0.1257 g gave 0.1352 g AgBr
0.1383 g gave 0.1485 g AgBr
0.2185 g gave 0.0088 g H_2O

	calc. for $Co_2N_7O_2H_{22}Br_3 \cdot H_2O$	found	
Co	22.15%	22.35%	22.28%
Br	45.50	45.70	45.65
H_2O	3.41	3.08	

C. Chloride:  $Cl_3 \cdot 1H_2O$

The chloride is prepared from the iodide or the bromide by triturating it with moist silver chloride and precipitating the salt from aqueous solution with absolute alcohol. It forms small, bright red needles. It is very soluble in water, forming neutral solutions.

0.1018 g gave 0.0796 g $CoSO_4$

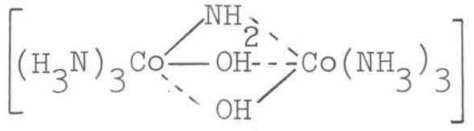
0.1028 g gave 0.0804 g $CoSO_4$

0.0957 g gave 0.1069 g AgCl

0.1094 g gave 0.1176 g AgCl

0.2830 g gave 0.0143 g H_2O

	calc. for $Co_2N_7O_2H_{22}Cl_3 \cdot H_2O$	found	
Co	29.90%	29.75%	29.79%
Cl	27.03	27.31	27.20
H_2O	4.55	5.04	

D. Nitrate:  $(NO_3)_3 \cdot 2H_2O$

One gram of iodide is triturated with a concentrated solution of 0.8 g of $AgNO_3$ and the silver iodide formed is filtered out of the red solution. The nitrate is precipitated as small red crystals by the addition of absolute alcohol. It is very soluble in water, giving a neutral solution.

0.1017 g gave 0.0638 g $CoSO_4$

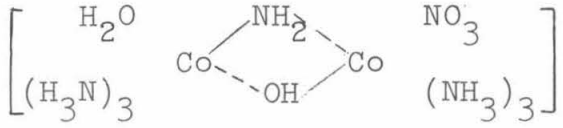
0.1042 g gave 0.0650 g $CoSO_4$

0.1089 g gave 28.15 ml Nitrogen at 21° and 728 mm pressure

0.2820 g gave 0.0171 g H_2O

	calc. for $Co_2N_{10}O_{11}H_{22} \cdot 2H_2O$	found		[93]
Co	23.78%	23.90%	23.78%	
N	28.46	28.18		
H_2O	7.30	6.06		

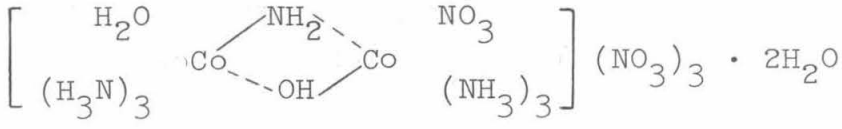
XX. Nitratoaquohexammine-μ-amido-μ-hydroxo dicobalt(III) salts



This series has been only cursorily examined[1] and has been

[1] Zeitschr. f. anorg. Chem. (1899) 21:108

designated as the nitrato hexammine-μ-imido dicobalt(III) series. Our recent more thorough investigation has completely clarified the constitution of this series.

A. Nitrate: 

This salt has been obtained previously in the following way. Diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate was dissolved in a little water while heating and the warm solution treated with an equal volume of concentrated nitric acid, whereupon the new salt crystallized out in yellow-brown plates. Since we needed large amounts of the salt for synthetic experiments, we have worked out a more detailed preparative method.

One gram of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate is dissolved in 7 ml of hot water to which a drop of nitric acid has been added. The solution is cooled somewhat and then mixed with 18 ml of concentrated nitric acid, whereupon the red color changes to brown-red. Within a few minutes the reaction product precipitates out as yellow-brown flat needles. The salt is filtered off after the solution has been allowed to stand for several hours. A large fraction of the nitrato salt remains in the brown-red solution. This is precipitated by cooling the solution with ice and then mixing it with alcohol. 43.8 g of nitratonitrate were obtained from 60 g of diaquo nitrate.

0.1291 g gave 0.0725 g $CoSO_4$ [94]

0.1328 g gave 34.8 ml Nitrogen at 19.5° and 710 mm pressure

	calc. for $Co_2N_{11}H_{23}O_{14} \cdot 2H_2O$	found
Co	21.24%	21.37%
N	27.80	27.89

B. On the effect of liquid ammonia on nitratoaquo-μ-amido-μ-hydroxo dicobalt(III) nitrate

by S. Malmgren

The reaction with liquid ammonia was carried out as follows: Sufficient liquid ammonia was added to 4 g portions of the nitrate in separate 3 cm reaction tubes to completely dissolve the salt. After the ammonia had evaporated, a red-brown solid residue remained which was extracted with cold water. The first extractions were

intensely red-brown colored; the last were lighter in color. The separate extractions were acidified with a little hydrochloric acid and treated with ammonium sulfate. Only a little insoluble sulfate precipitated from the first extraction, while large amounts of this sulfate came out of the last two. The insoluble sulfates, which have a reddish color, were combined and converted into the nitrate by triturating with an excess of ammonium nitrate in a little water. The reaction product was washed free of ammonium nitrate with water, then dissolved in water and treated with ammonium bromide, giving a fire-red, finely crystallized bromide precipitate. The analysis of this bromide showed that the salt was octammine-μ-amido-μ-hydroxo dicobalt(III) bromide.

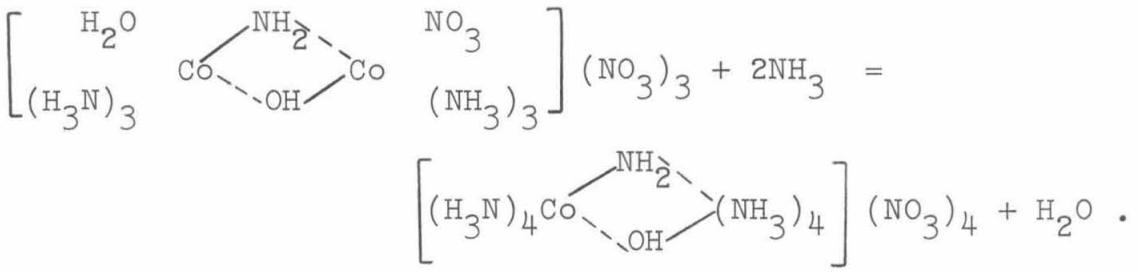
0.0668 g gave 0.312 g $CoSO_4$

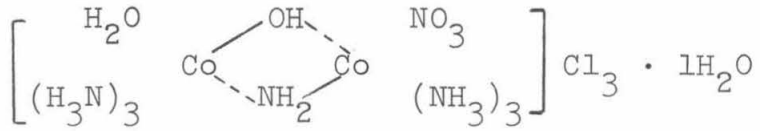
0.1489 g gave 26.2 ml Nitrogen at 22° and 724 mm pressure

0.1188 g gave 0.1350 g AgBr

	calc. for $Co_2N_9OH_{27}Br_4 \cdot 3H_2O$	found
Co	17.85%	17.81%
N	19.06	18.88
Br	48.41	48.39

As is evident from the above, the effect of liquid ammonia on nitratoaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate [95] is to produce octammine-μ-amido-μ-hydroxo dicobalt(III) nitrate. This conversion can be expressed by the following equation:



C. Chloride: 

The nitrate is dissolved in cold water and the cold aqueous solution carefully treated with a little concentrated hydrochloric acid. On cooling, the chloride crystallizes out in lustrous, chamois colored, silky flat needles. The salt is filtered off as rapidly as possible because the color of the solution darkens if it is allowed to stand for any length of time, probably due to the formation of chloro salts.

0.0401 g gave 0.0276 g $CoSO_4$

0.0484 g gave 0.0458 g AgCl

0.0551 g gave 12.2 ml Nitrogen = 13.4 mg

	calc. for $Co_2N_8H_{23}O_5Cl_3 \cdot 1H_2O$	found
Co	26.00%	26.20%
N	24.40	24.30
Cl	23.20	23.30

This salt is quite soluble in water, forming a yellow-brown solution.

D. Bromide: $\left[(H_3N)_3 \; H_2O \; \underset{\diagdown OH \diagup}{\overset{\diagup NH_2 \diagdown}{Co}} \; Co \; (NH_3)_3 \; NO_3 \right] Br_3 \cdot 1H_2O$

The nitrate is dissolved in cold water and the resulting solution is quickly filtered and treated with solid ammonium bromide. A slurry of flesh-colored, silvery, very small flat needles forms after a few minutes. The bromide is also obtained when an ice-cold solution of the nitrate is treated with hydrobromic acid. A thick, matted flesh-colored lustrous mass is obtained when the salt is filtered out.

0.1014 g gave 0.0199 g $CoSO_4$ [96]
0.1006 g gave 0.0530 g $CoSO_4$
0.1164 g gave 0.1059 g AgBr
0.1025 g gave 17.6 ml Nitrogen at 17.5° and 721.5 mm
0.1892 g lost 0.0056 g at 100°

	calc. for $Co_2N_8O_5H_{23}Br_3 \cdot 1H_2O$	found	
Co	19.96%	19.62%	19.93%
N	19.22	18.76	
Br	40.60	39.52	
H_2O	3.14	2.96	

XXI. Tetrachlorohexammine-μ-amido and trichloroaquohexammine-μ-amido dicobalt(III) salts

A. Chloride:

$\left[\begin{matrix} Cl_2 \\ (H_3N)_3 \end{matrix} \; Co\text{-}NH_2\text{-}Co \; \begin{matrix} Cl_2 \\ (NH_3)_3 \end{matrix} \right] Cl$ and $\left[\begin{matrix} Cl_2 \\ (H_3N)_3 \end{matrix} \; Co\text{-}NH_2\text{-}Co \; \begin{matrix} Cl \\ OH_2 \\ (NH_3)_3 \end{matrix} \right] Cl_2$

(Melanochloride)

If concentrated hydrochloric acid is added to a warm solution of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate, its color quickly changes to greenish-brown and a lustrous violet-black salt crystallizes out in microscopic hexagonal platelets. It is very difficultly soluble in water, initially forming a brown solution that quickly changes to red. The red solution is acidic.

The salt gives the following analytical results after being dried at 60-65°.

0.0500 g gave 0.0374 g $CoSO_4$

0.1000 g gave 0.1733 g AgCl

0.0500 g gave 10.6 ml Nitrogen at 15° and 725 mm pressure

0.1000 g gave 0.0440 g H_2O

	calc. for $Co_2N_7H_{20}Cl_5$	found
Co	28.30%	28.36%
N	23.72	23.60
H	4.85	4.89
Cl	42.84	42.77

The essentials of the behavior of the salt towards various reagents have been reported previously.[1]

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[1]Zeitschr. f. anorg. Chem. (1898) 16:163

If the salt is dried at 60-65°, but is instead analyzed directly as it is obtained, it is found that it contains one additional molecule of water and only three nonionically bonded [97]

chlorine atoms, as could be demonstrated by the preparation of the nitrate. There is no difference in appearance between the two salts.

0.1460 g gave 0.1048 g $CoSO_4$

0.1513 g gave 0.2525 g AgCl

	calc. for $Co_2N_7H_{22}OCl_5$	found
Co	27.35%	27.31%
Cl	41.14	41.26

B. Trichloronitrato hexammine-μ-amido dicobalt(III) nitrate

$$\left[\begin{matrix} Cl_2 & & Cl \\ & Co\text{-}NH_2\text{-}Co & NO_3 \\ (H_3N)_3 & & (NH_3)_3 \end{matrix} \right] NO_3$$

If the trichloro chloride just described is triturated twice with concentrated nitric acid, dissolved in cold water with thorough shaking and immediately treated with nitric acid, a violet-black crystalline salt is obtained which has only three chlorine atoms bonded to each pair of cobalt atoms.

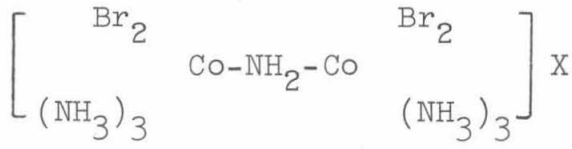
0.1473 g gave 0.0981 g $CoSO_4$

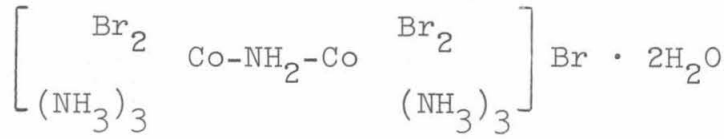
0.1576 g gave 0.1458 g AgCl

	calc. for $Co_2N_9H_{20}O_6Cl_3$	found
Co	25.30%	25.33%
Cl	22.84	22.87

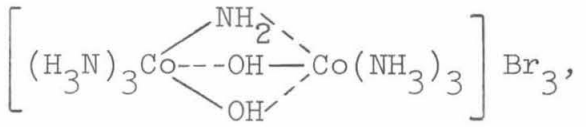
The nitrate is much more soluble in water than the chloride from which it was prepared.

XXII. Tetrabromohexammine-μ-amido dicobalt(III) salts



A. Bromide: 

This compound is prepared by heating an aqueous solution of hexammine-μ-amido-di-μ-hydroxo dicobalt(III) bromide,

 [98]

with concentrated hydrobromic acid in a water bath. It is a brown-green powder consisting of very small crystals. It is insoluble in cold water.

0.0950 g gave 0.0442 g $CoSO_4$

0.1140 g gave 0.0532 g $CoSO_4$

0.1002 g gave 0.1418 g AgBr

0.1892 g lost 0.0077 g H_2O at 100°

	calc.	found	
Co	17.55%	17.70%	17.76%
Br	59.57	60.02	
H_2O	5.52	4.18	

The salt loses both molecules of water on being dried at 70-80°.

B. Nitrate: $\left[\begin{matrix} Br_2 & & Br_2 \\ & Co\text{-}NH_2\text{-}Co & \\ (H_3N)_3 & & (NH_3)_3 \end{matrix} \right] NO_3 \cdot 2H_2O$

The nitrate is prepared by triturating the bromide with half-saturated nitric acid and the salt quickly filtered out. This operation is repeated two or three times. The nitrate is completely similar to the bromide in appearance.

I. J. Fürstenberg

0.1150 g gave 0.0524 g $CoSO_4$

0.1004 g gave 0.0475 g $CoSO_4$

0.1104 g gave 0.1259 g AgBr

0.1325 g gave 0.1513 g AgBr

0.1871 g lost 0.0114 g H_2O at 80°

II. M. Grigorieff

0.1038 g gave 0.0499 g $CoSO_4$

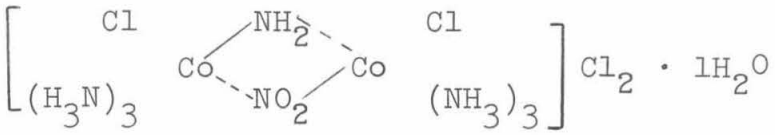
0.0995 g gave 15.9 ml Nitrogen at 20° and 729.5 mm pressure

0.1152 g gave 0.1322 g AgBr

	calc.	found	
		I	II
Co	18.04%	17.88% 18.00%	18.20%
Br	48.95	48.53 --	48.78
H_2O	6.02	6.02 --	--
N	17.12	-- 17.41	--

XXIII. Dichlorohexammine-μ-amido-μ-nitrito dicobalt(III) salts [99]

$\left[\begin{matrix} Cl & & Cl \\ & Co \begin{matrix} \diagup NH_2 \\ \diagdown NO_2 \end{matrix} Co & \\ (H_3N)_3 & & (NH_3)_3 \end{matrix} \right] X_2$

A. Chloride: 

One gram of tetraaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate is mixed with 0.25 g sodium nitrite and covered with a little water. On heating, an orange colored solution is produced to which concentrated hydrochloric acid is added as soon as all the solid has dissolved. A reddish-brown salt crystallizes out in the form of micaceous flakes accompanied by the rigorous evolution of nitrous oxides. The salt can be purified by dissolving it in warm water, filtering the solution and adding concentrated hydrochloric acid to it. It has been shown to be identical to the salt described earlier[1]

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[1]Zeitschr. f. anorg. Chem. (1898) 16:749 *

*Translator's Note: As volume 16 has but 488 pages, Werner probably means 16:116.

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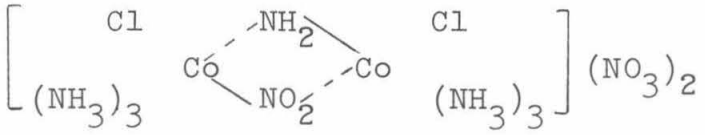
as hexammine-μ-(hydronitritoimido) dicobalt(III) chloride, which was prepared from the Melano chloride.

0.1016 g gave 0.0708 g $CoSO_4$

0.1002 g gave 0.0270 g $CoSO_4$

0.0998 g gave 23.0 ml Nitrogen at 18.5° and 721 mm pressure

	calc.	found	
Co	26.70%	26.62%	26.94%
N	25.35	25.02	

B. Nitrate: 

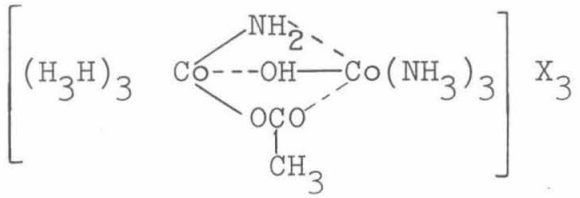
The chloride was triturated with concentrated nitric acid and the reaction product washed free of acid with alcohol on a clay plate. The dried product was then dissolved in cold water and the nitrate precipitated from the filtered solution by the addition of concentrated nitric acid. The salt was obtained in the form of a red-brown crystalline powder having an ochre-colored appearance. It is moderately soluble in water.

0.1502 g gave 0.0969 g $CoSO_4$ [100]

0.1696 g gave 0.0988 g AgCl

	calc. for $Co_2N_{10}H_{12}O_8Cl_2$	found
Co	24.75%	24.55%
Cl	14.85	14.46

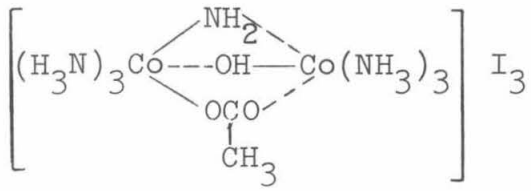
XXIV. Hexammine-μ-amido-μ-hydroxo-μ-acetato dicobalt(III) salts



by J. Fürstenberg

In the investigation of the hexammine-μ-amido-di-μ-hydroxo dicobalt(III) salts, the very interesting and theoretically important observation has been made that the acetate group has

the property of taking the place of a hydroxyl bridge. The acetate group is very strongly bound and, consequently, the properties of the parent molecule appear to be profoundly altered. This is especially evident in that the salts do not undergo the so-called Melano reaction, i.e., black Melanochloride does not precipitate from an aqueous hydrochloric acid solution of the salt.

A. Iodide: 

A solution of diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate is heated with acetic acid in a water bath and then is treated with an excess of potassium iodide. Long, vivid red prismatic needles or lustrous flakes precipitate from the cooled solution. The salt is difficultly soluble in water, but quite soluble in warm acetic acid. Since it is easily purified, it has been used as the starting material in the preparation of the other salts. The aqueous solution is neutral.

0.1145 g gave 0.0514 g $CoSO_4$ [101]

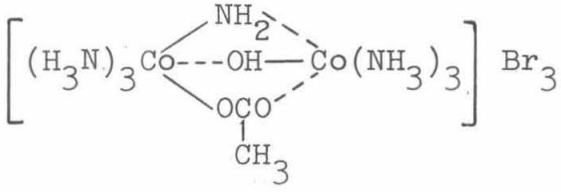
0.1014 g gave 0.0456 g $CoSO_4$

0.1147 g gave 0.1120 g AgI

0.1032 g gave 0.1049 g AgI

0.1979 g gave 0.0247 g CO_2 and 0.0624 g H_2O

	calc. for $Co_2N_7C_2H_{24}O_3I_3$	found	
Co	17.03%	17.07%	17.12%
I	55.1	55.05	55.65
C	3.46	3.47	
H	3.46	3.51	

B. Bromide: 

The bromide can be prepared from the iodide with silver bromide. One g of iodide was triturated with 2 g of moist, well washed silver bromide and heated to 40°. After the silver iodide has been filtered out, the bromide is precipitated from the solution as bright red needles by the addition of absolute alcohol. The salt dissolves in water to give a neutral solution

0.1155 g gave 0.0658 g $CoSO_4$

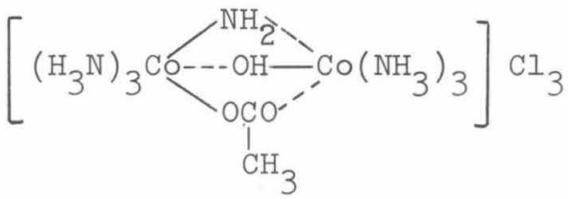
0.1272 g gave 0.7200 g $CoSO_4$

0.0918 g gave 0.0949 g AgBr

0.1102 g gave 0.1134 g AgBr

0.1155 g gave 0.0183 g CO_2

	calc. for $Co_2N_7C_2H_{24}O_3Br_3$	found	
Co	21.38%	21.65%	21.54%
Br	43.46	44.00	43.79
C	4.35	4.30	

C. Chloride: 

This salt was prepared from the iodide. One gram of the iodide was ground with wll washed, moist silver chloride, the silver iodide removed and the salt precipitated by addition of alcohol. The chloride forms bright red needles that can be easily dissolved in water. Solutions of the chloride are neutral.

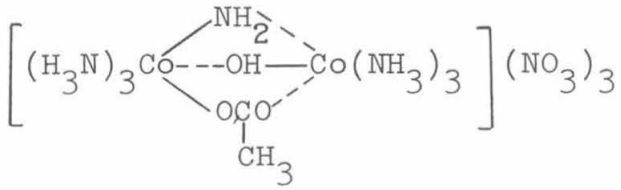
0.1248 g gave 0.0918 g $CoSO_4$ [102]

0.1120 g gave 0.0828 g $CoSO_4$

0.1474 g gave 0.1502 g AgCl

0.1192 g gave 0.0251 g CO_2

	calc. for $Co_2N_7C_2H_{24}O_3Cl_3$	found
Co	28.19%	27.99%
Cl	25.51	25.29
C	5.73	5.68

D. Nitrate: 

The nitrate was obtained from the iodide. One g of iodide was triturated with 0.8 g $AgNO_3$ in solution. After the silver iodide had been filtered out, the nitrate was precipitated from the solution with absolute alcohol.

The nitrate precipitates as a bright red, finely crystalline powder which is quite soluble in water and forms neutral solutions.

0.0994 g gave 0.0612 g $CoSO_4$

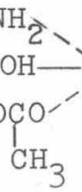
0.1094 g gave 0.0669 g $CoSO_4$

0.1086 g gave 27.8 ml Nitrogen at 21° and 723 mm pressure

0.1115 g gave 0.0183 g CO_2

	calc. for $Co_2N_{10}C_2H_{24}O_{12}$	found	
Co	23.68%	23.43%	23.46%
N	28.14	27.84	
C	4.82	4.63	

E. <u>Chloroplatonate</u>: $\left[(H_3N)_3Co\begin{matrix}\diagup NH_2 \diagdown \\ \diagdown OH \diagup \\ \diagup OCO \diagdown \end{matrix}Co(NH_3)_3\right]_2(PtCl_4)_3$



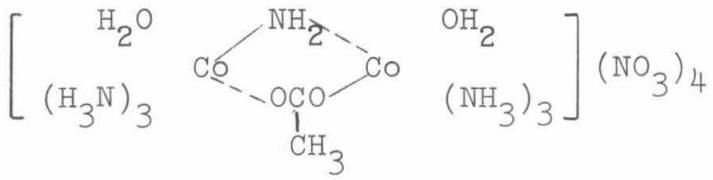
A solution of the chloride is prepared by grinding the iodide with moist AgCl; this is then mixed with potassium platinum(II) chloride. Highly reflective, bright red crystals of platinum(II) chloride adduct precipitate out after a few minutes.

0.1748 g gave 0.0642 g Pt and 0.0662 g $CoSO_4$

0.1405 g gave 0.0152 g CO_2

	calc. for $Co_4N_{14}C_4H_{48}O_6Pt_3Cl_{12}$	found
Co	14.46%	14.5%
Pt	36.62	36.9
C	2.97	3.01

XXV. Diaquohexammine-μ-amido-μ-acetato dicobalt(III) salts [103]

A. Nitrate: 

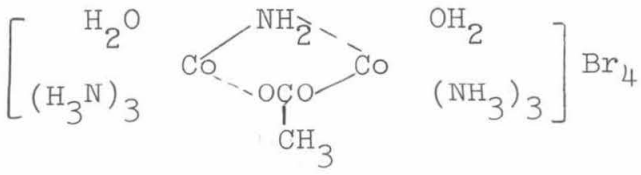
One g of glacial acetic acid is added to a solution of hexammine-μ-amido-di-μ-hydroxo dicobalt(III) nitrate and this is then heated to 70°. The new salt is precipitated from the cooled solution as lustrous, bright red crystalline plates by the addition of concentrated nitric acid. The nitrate is quite soluble in water, giving an acidic solution which corresponds in its properties to those of all the aquocobalt(III) ammines.

0.1345 g gave 0.0726 g $CoSO_4$

0.1210 g gave 0.0654 g $CoSO_4$

0.1082 g gave 28.4 ml Nitrogen at 20° and 726 mm pressure

	calc. for $Co_2N_{11}C_2O_{16}H_{27}$	found	
Co	20.40%	20.55%	20.57%
N	26.60	26.70	

B. Bromide: 

Forty per cent hydrobromic acid was added to a cold solution of the nitrate until the small red crystals of the bromide stopped precipitating.

0.1300 g gave 0.0619 g $CoSO_4$

0.1227 g gave 0.0590 g $CoSO_4$

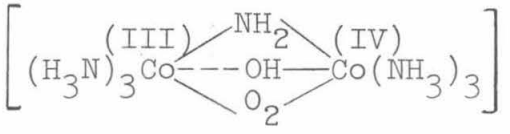
0.1398 g gave 0.1612 g AgBr

	calc. for $Co_2N_7C_2O_4H_{27}Br_4$	found	
Co	18.13%	18.10%	18.30%
Br	49.15	49.10	

The salt dissolves in water to give a strongly acidic solution.

XXVI. Hexammine-μ-amido-μ-hydroxo-μ-peroxo dicobalt(III,IV) salts

by M. Grigorieff



[104]

This series of compounds is identical to the series designated as ozoimidohexammine dicobalt(III) salts[1,*] which has previously

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[1]Zeitschr. f. anorg. Chem. (1899) 21:109

*Translator's note: This is a synonym for hexammine-μ-imido-μ-peroxo dicobalt(III) salts.

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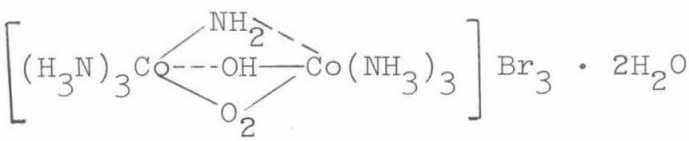
been only cursorily investigated because of a lack of material.

A. Bromide: 

The black chloride obtained from solution A,* which was prepared

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*Translator's note: See p. 89 in original, p. 124 in translation for the preparation of "solution A".

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in the processing of the crude Melanochloride to obtain diaquohexammine-μ-amido-μ-hydroxo-dicobalt(III) salts, serves as the starting material in the preparation of these salts.

About 10 g of the black chloride is ground with a concentrated solution of 12 g of $AgNO_3$ which has been acidified with a drop of HNO_3 and the mixture heated slightly.

The deep brown-black solution is filtered and the silver chloride precipitate extracted with small amounts of water which have been heated to 50°. The combined solutions yield red crystals after standing for several hours. These are filtered off. The solution is then saturated with solid ammonium bromide at room temperature, yielding approximately 3 g of a dark green salt on being cooled. A brown bromide is precipitated from the remaining solution by the addition of alcohol.

The green salt is purified by dissolving it in the minimum amount of water heated to 40° to which a drop of acetic acid has been added and then allowing it to recrystallize in a desiccator. After a few hours, large black-green needles of the pure bromide have formed. The salt is easily dissolved in water, giving a neutral solution.

0.1516 g gave 0.0844 g $CoSO_4$ [105]

0.1183 g gave 0.0674 g $CoSO_4$

0.1036 g gave 0.1039 g AgBr

0.1243 g gave 0.1247 g AgBr

0.1678 g lost 0.0114 g H_2O at 80°

	calc. for $Co_2N_7O_3H_{21}Br_3 \cdot 2H_2O$	found	
Co	21.03%	21.18%	21.16%
Br	42.78	42.65	42.66
H_2O	6.41	6.42	

Hexammine-μ-amido-μ-hydroxo-μ-peroxo dicobalt(III,IV) bromide can also be obtained from octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate according to the following method.

About 1 g of octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate is heated with 1 g of ammonium chloride in about 5 ml of water over an open flame until the color of the solution has changed from green to brown and a red-violet salt begins to precipitate on the wall of the reaction vessel. Ammonia is liberated in this reaction; this is easily recognized by its odor. The filtered brown solution is then treated with four or five times its volume of hydrochloric acid while being heated slightly and it is then allowed to stand for a while. A finely crystallized brown to black salt which is still a mixture settle out. This is processed in the following way.

A very concentrated solution containing about 1 g of chloride and 1.5 g of silver nitrate is boiled and the resulting brown-green solution filtered free of silver chloride. The silver chloride must be well washed. The resulting solution is now treated with much

ammonium bromide and ground until the green salt has precipitated completely and the solution has taken on a distinctly red color.

The green bromide is dissolved in the minimum amount of hot water and then, after the silver bromide has been filtered out, is reprecipitated by further addition of ammonium bromide. If the solution should become too dilute, the bromide can be precipitated by adding alcohol. The bromide is pure after one [106] such recrystallization from aqueous solution containing some acetic acid. It was proved to be identical to that described above.

0.3463 g gave 0.0224 g H_2O (at 75-80°)

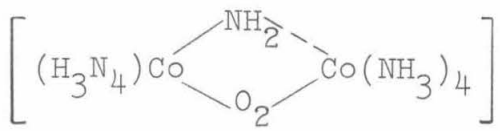
	calc. for $Co_2N_7O_3H_{21}Br_3 \cdot 2H_2O$	found
H_2O	6.41%	6.46%

Analysis of the anhydrous compound:

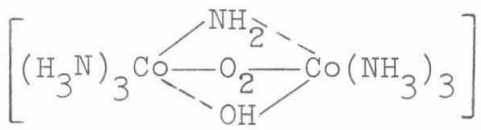
0.1119 g gave 0.0657 g $CoSO_4$
0.1073 g gave 0.0627 g $CoSO_4$
0.1119 g gave 19.8 ml Nitrogen at 19° and 715 mm pressure
0.1172 g gave 0.1257 g AgBr

	calc. for $Co_2N_7O_3H_{21}Br_3$ (anhydrous)	found	
Co	22.47%	22.34%	22.29%
N	18.66	18.94	
Br	45.71	45.2	

The conversion of octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate into the hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) salts can be formulated in the following way:

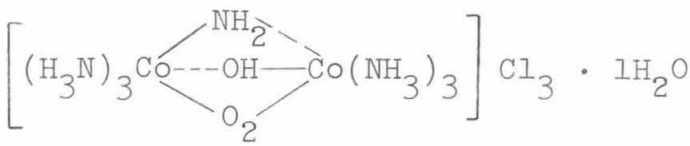


$$\left[(H_3N_4)Co(NH_2)_2Co(NH_3)_4\right](NO_3)_4 + H_2O =$$



$$\left[(H_3N)_3Co(NH_2)(O_2)(OH)Co(NH_3)_3\right](NO_3)_3 + HNO_3 + 2NH_3$$

B. <u>Chloride</u>:



$$\left[(H_3N)_3Co(NH_2)(OH)(O_2)Co(NH_3)_3\right]Cl_3 \cdot 1H_2O$$

The chloride is prepared from the bromide by agitating a concentrated bromide solution with freshly precipitated silver chloride for 2 - $2\frac{1}{2}$ hours. The silver bromide-silver chloride mixture is filtered out of the solution, which is then treated with either ammonium chloride or with alcohol to precipitate the chloride. The salt is recrystallized from a little water.

0.1021 g gave 0.0772 g $CoSO_4$

0.1150 g gave 26.6 ml Nitrogen (dry) at 22° and 728.5 mm pressure

	calc. for $Co_2N_7O_3H_{21}Cl_3 \cdot 1H_2O$	found
Co	28.82%	28.79%

0.1092 g gave 0.1198 g dry AgCl [107]

	calc. for $Co_2N_7O_3H_{21}Cl_3$ (water-free)	found
N	25.06%	24.98%
Cl	27.02	27.01

C. Nitrate: $\left[(H_3N)_3Co\begin{matrix}\diagup NH_2\diagdown\\ -O_2-\\ \diagdown OH\diagup\end{matrix}Co(NH_3)_3\right](NO_3)_3 \cdot 1H_2O$

The bromide can be transformed into the nitrate by reaction with the stoichiometric amount of silver nitrate in cold aqueous solution. Once the silver bromide has been filtered out of the solution, the nitrate is precipitated in the form of beautiful, highly refractive dark green flakes by the addition of alcohol.

The nitrate also often crystallizes from the first aqueous extraction when the crude Melanochloride is worked up with silver nitrate, forming fairly large, six-sided, dark green plates.

0.1106 g gave 0.0702 g $CoSO_4$

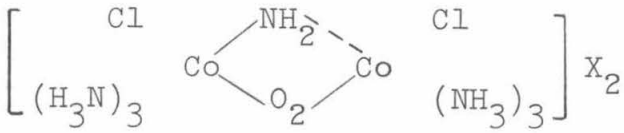
0.1109 g gave 0.0701 g $CoSO_4$

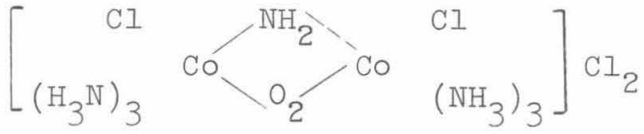
	calc. for $Co_2N_{10}O_{12}H_{21}Cl_3 \cdot 1H_2O$	found	
Co	24.13%	24.14%	24.07%

0.1122 g gave 31.2 ml dry Nitrogen at 22° and 725 mm pressure

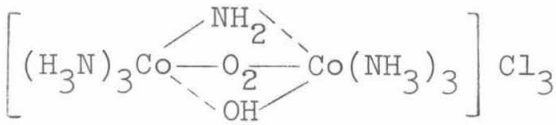
	calc. for $Co_2N_{10}O_2H_{21}Cl_3$ · (anyhydrous)	found
N	29.72%	29.86%

XXVII. Symmetric dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) salts



A. Chloride: 

If an aqueous solution of the hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) chloride,



is treated with concentrated hydrochloric acid and heated, a voluminous black crystalline salt precipitates out which is only very slightly solube in water. The salt, as has already been shown,[1] can also be prepared from the nitrate using the same [108]

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[1]Zeitschr. f. anorg. Chem. (1899) 21:111

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procedure.

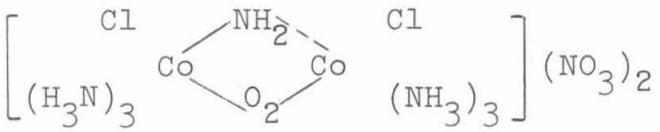
Salt dried for a long time in a desiccator is anhydrous.

0.0984 g gave 0.0744 g $CoSO_4$

0.1212 g gave 27.2 ml Nitrogen at 23° and 721 mm pressure

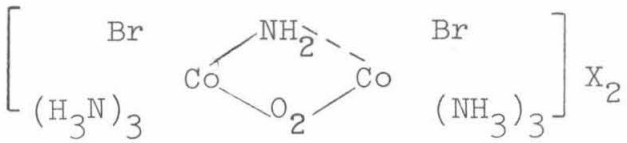
0.0976 g gave 0.0838 g AgCl

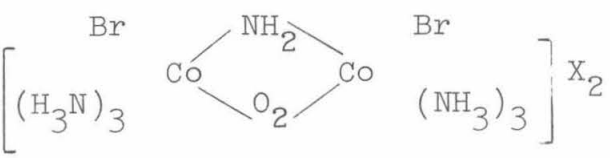
	calc. for $Co_2N_7O_2H_{20}Cl_4$	found
Co	28.80%	28.75%
N	23.92	23.82
Cl	34.57	34.63

B. Nitrate: 

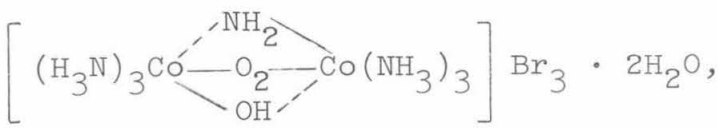
This nitrate is obtained if the chloride is triturated with concentrated nitric acid several times. The nitrate is so similar in appearance to the chloride that they are easily confused. It is also only very slightly soluble in water.

XXVIII. Symmetric dibromohexammine-μ-amido-μ-peroxo dicobalt(III,IV) salts



A. Bromide: 

If a solution of hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) bromide,



is treated with concentrated hydrobromic acid and heated slightly, a green-black salt separates out as small, flat, very shiny crystals. The new salt is almost insoluble in water.

The freshly prepared salt lost not quite 1/2 molecule of water [109] on drying, probably because it had not yet been completely dried.

0.1114 g gave 0.0584 g $CoSO_4$

0.1097 g gave 16.8 ml Nitrogen at 23° and 730 mm pressure

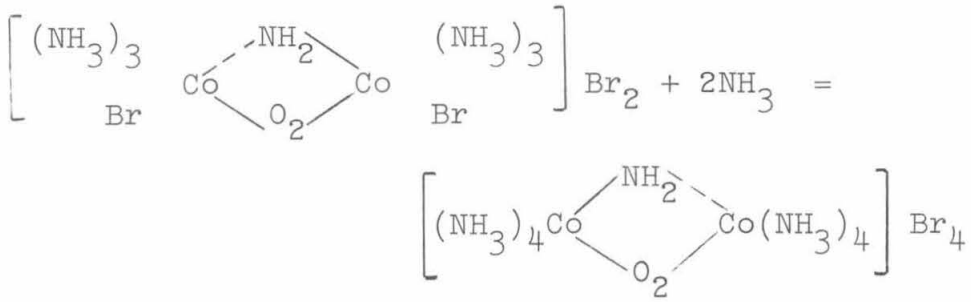
0.1179 g gave 0.1525 g AgBr

	calc. for $Co_2N_7O_2H_{20}Br_4$	found
Co	20.06%	19.92%
N	16.66	16.49
Br	54.42	54.96

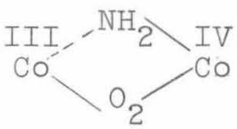
B. <u>The effect of anyhdrous ammonia on symmetric dibromo-hexammine-μ-amido-μ-peroxo dicobalt(III,IV) bromide</u>

If a sample of the bromide just described is covered with sufficient liquid ammonia in a wide reaction tube so as to completely dissolve it, a greenish-brown solution results which, upon the evaporation of the ammonia, gives a brownish residue that is very soluble in water. If an aqueous solution of this substance is treated with some dilute sulfuric acid, an insoluble, silvery, pale-green sulfate immediately precipitates out. If this sulfate is ground with some concentrated nitric acid, octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate is obtained, which is easily recognized from its characteristic properties.

Liquid ammonia consequently reacts according to the following equation:



It has thus been shown synthetically that the octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts contain the same molecular nucleus

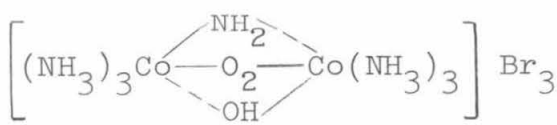


as the hexammine-μ-amido-μ-peroxo dicobalt(III,IV) salts:

C. <u>On the reduction of the hexammine-μ-amido-μ-peroxo dicobalt(III,IV) salts</u> [110]

by M. Grigorieff

The conversion of hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) salts into hexammine-μ-amido dicobalt(III) salts is begun with hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) bromide,



The reduction is easily carried out with sulfurous acid by the following method. One g of bromide is covered with a saturated aqueous SO_2 solution and heated carefully until the resulting

solution takes on a brownish-red color. Heating until the color changes to brick red must be avoided because decomposition occurs easily. The brown-red solution is immediately treated with concentrated hydrobromic acid and heated slightly, giving a precipitate of the green-black tetrabromohexammine-μ-amido dicobalt(III) bromide:

$$\left[\begin{matrix} Br_2 & & Br_2 \\ & Co\text{-}NH_2\text{-}Co & \\ (H_3N)_3 & & (NH_3)_3 \end{matrix} \right] Br \ .$$

This bromide can be transformed into the nitrate by heating it with the stoichiometric amount of silver nitrate in weak nitric acid solution. Most of the salt can be precipitated by cooling the solution.

0.0999 g gave 0.0548 g $CoSO_4$

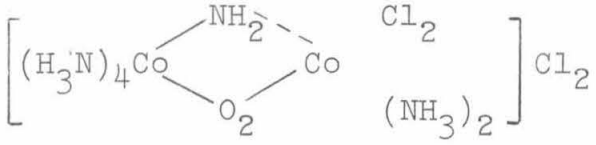
0.1014 g gave 24.8 ml Nitrogen at 19° and 727 mm pressure

	calc. for $Co_2N_{11}O_{15}H_{25} \cdot 2H_2O$	found
Co	20.59%	20.88%
N	26.87	26.95

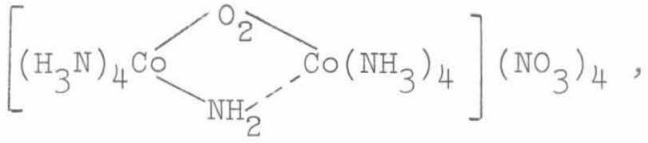
Diaquohexammine-μ-amido-μ-hydroxo dicobalt(III) nitrate has been obtained in the previously described manner as the reduction product of hexammine-μ-amido-μ-peroxo-μ-hydroxo dicobalt(III,IV) bromide:

$$\left[(NH_3)_3Co \begin{matrix} \diagup NH_2 \diagdown \\ -O_2- \\ \diagdown OH \diagup \end{matrix} Co(NH_3)_3 \right] Br_3 \rightarrow \left[\begin{matrix} (NH_3)_3 & & (NH_3)_3 \\ & Co \begin{matrix} \diagup NH_2 \diagdown \\ \diagdown OH \diagup \end{matrix} Co & \\ H_2O & & OH_2 \end{matrix} \right] (NO_3)_4 \cdot$$

XXIX. Unsymmetric dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) chloride [111]



Five g of air-dried octammine-μ-amido-μ-peroxo dicobalt(III,IV) nitrate,



is stirred with 25 ml of cold water in a beaker and 5 g of pulverized ammonium carbonate is added to the mixture. This is then heated over an open flame with constant shaking until the color of the solution has changed from olive green to brown-red. The solution is then filtered into an ice cold porcelain dish. When the solution has been well cooled, 20 ml of concentrated hydrochloric acid are added dropwise with constant stirring, resulting in the vigorous evolution of CO_2.

Granular, dark olive green crystals soon precipitate and almost completely cover the bottom of the dish. The contents of the dish are allowed to stand about 20 minutes at room temperature and are then suction filtered. If the solution is allowed to stand longer, a brown substance precipitates in addition to the green salt. The green chloride is reprecipitated from a cold aqueous solution by the addition of concentrated hydrochloric acid, after which it is washed with alcohol and ether. Yield: 1 gram.

I. 0.1008 g gave 0.0758 g $CoSO_4$

0.1174 g gave 0.1622 g AgCl

0.1030 g gave 22.6 ml Nitrogen at 26° and 722 mm pressure

II. Analysis of the reprecipitated salt

0.1002 g gave 0.7560 g $CoSO_4$

0.1006 g gave 21.6 ml Nitrogen at 26° and 721 mm pressure

0.1072 g gave 0.1492 g AgCl

	calc. for $Co_2N_7O_2H_{20}Cl_4$	found I	found II
Co	28.84%	28.61%	28.70%
N	23.53	23.79	23.89
Cl	34.66	34.16	34.42

[112]

The chloride is quite soluble in water, giving an intensively brown colored solution.

A. Cleavage of the chloride with hydrochloric acid

When the chloride is covered with dilute hydrochloric acid and heated for a while over an open flame, a deep-blue solution is formed with vigorous evolution of chlorine. A purple crystalline salt precipitates when the solution is cooled.

If the cleavage is to be carried out as smoothly as possible, the following conditions must hold: 60 ml of half-strength hydrochloric acid is poured over 1 g of chloride and the mixture is heated at a not-too-high temperature only until all of the green salt is dissolved. The heating is then stopped and a few drops of water are added to the solution, whereupon its color

changes from blue to pink, and copious precipitate of the purple salt forms. This salt is almost insoluble in cold dilute hydrochloric acid. After the solution has cooled, the precipitate is removed by suction filtration and is washed repeatedly with alcohol and ether. The salt can be recrystallized from weak aqueous acetic acid solution. Small purple-red crystals are thus obtained which, as shown by the analysis, consist of chloropentammine cobalt(III) chloride.

0.1018 g gave 0.0630 g $CoSO_4$

0.1062 g gave 27.0 ml Nitrogen at 24° and 733 mm pressure

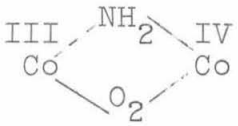
0.1296 g gave 0.2228 g AgCl

	calc. for $CoN_5H_{15}Cl_3$	found
Co	23.55%	23.54%
N	27.97	28.18
Cl	42.50	42.48

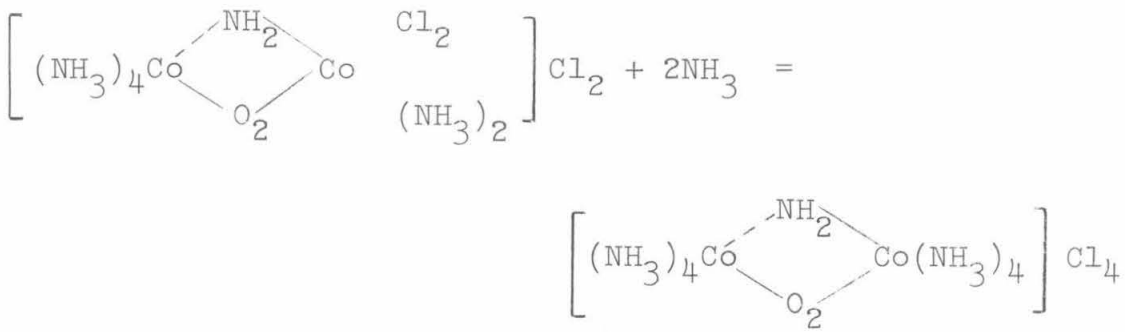
B. On the effect of liquid ammonia on unsymmetric dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) chloride [113]

Liquid ammonia is poured over the chloride in a wide reaction tube, very quickly giving a dirty-brown colored solution. A greenish-brown residue that is very soluble in water remains after the ammonia has evaporated. If an aqueous solution of this residue is treated with a little dilute sulfuric acid, large amounts of micaceous crystals of an insoluble green-black sulfate precipitate out. This salt, as is easily shown by its conversion into the

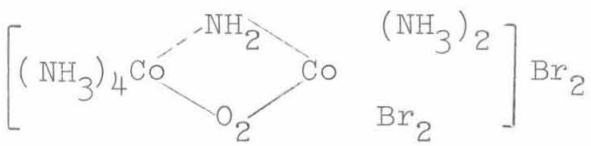
corresponding nitrate and its other properties, is octammine-μ-amido-μ-peroxo dicobalt(III,IV) sulfate. It is thus evident that the unsymmetrical dichloro series just described possesses the same molecular nucleus,



as the octammine-μ-amido-μ-peroxo dicobalt(III,IV) salts. The conversion from the unsymmetric dichloro series to the octammine series must therefore be formulated as follows:



C. Bromobromide:



For the preparation of this salt an aqueous solution of the chlorochloride is treated with the stoichiometric amount of ammonium bromide, giving small, lustrous, black-brown needle-like crystals after a short time. These are suction filtered from the mother liquor. In order not to lose too much material, the mother liquor is cooled and concentrated hydrobromic acid is added to it, yielding another rich precipitation of salt. [114]

The salt resulting from the ammonium bromide treatment is dissolved in a little water and precipitated with fuming hydrobromic acid in order to purify it. It is then sucked dry and washed with alcohol and ether. The yield from 1 g of chloride is about 0.8-0.9 g of bromide.

0.1040 g gave 0.0550 g $CoSO_4$

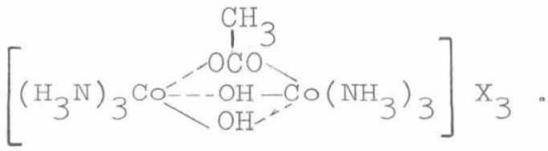
0.1094 g gave 0.1406 g AgBr

0.1026 g gave 15.80 ml Nitrogen at 23° and 726 mm pressure

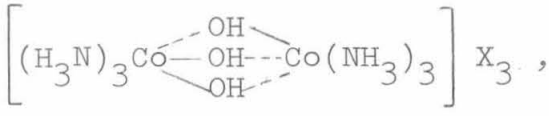
	calc. for $Co_2N_7O_2H_{20}Br_4$	found
Co	20.06%	20.12%
N	16.65	16.96
Br	54.42	54.69

The bromobromide is quantitatively converted into octammine-μ-peroxo dicobalt(III,IV) salt by liquid ammonia. The experimental procedure for this reaction is the same as that for the chloro chloride.

XXX. Hexammine-μ-acetato-di-μ-hydroxo dicobalt(III) salts



This series of compounds is obtained from the hexammine-tri-μ-hydroxo dicobalt(III) series,



which has been thoroughly described and its constitution inconstestably proven in an earlier report.[1] We can therefore

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[1]Ber. d. d. chem. Ges. (1907) 40:4834

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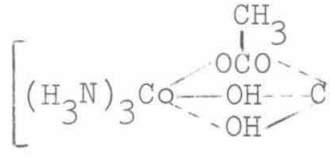
immediately set about to describe the μ-acetato series derived from it.

A. Chloride:  [115]

If a concentrated aqueous solution of hexammine-tri-μ-hydroxo dicobalt(III) chloride to which glacial acetic acid has been added is evaporated in a water bath and then cooled, long red needles crystallize from the resulting syrupy solution. This salt differs from the original chloride in having a more violet color. The product is sucked dry and washed free of adhering acetic acid with alcohol and then finally with ether. The salt thus prepared is extraordinarily soluble in water, so much so that the acetic acid solution must be well evaporated if a good yield is desired.

0.0830 g air dried salt gave 0.0527 g $CoSO_4$

0.1029 g gave 15.8 ml Nitrogen at 15° and 718 mm pressure

	calc. for $Co_2N_6Cl_8C_2O_4H_{23} \cdot 4H_2O$	found
Co	24.00%	24.16%
N	17.09	16.95

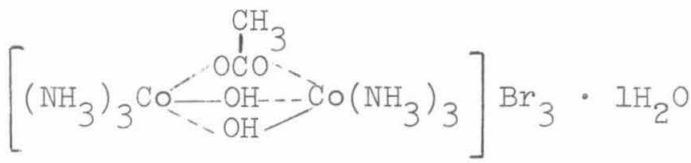
The salt loses three molecules of water on drying at 100-110°. The analysis of this dried salt gives the following results:

0.1000 g gave 0.0689 g $CoSO_4$

0.1000 g gave 17.5 ml Nitrogen at 17° and 726 mm pressure

0.1000 g gave 0.1010 g AgCl

	calc. for $Co_2N_6Cl_3O_4H_{23} \cdot 1H_2O$	found
Co	26.28%	26.56%
N	19.20	19.36
Cl	24.35	24.97

B. Bromide: 

A solution of hexammine-tri-μ-hydroxo dicobalt(III) bromide and acetic acid is evaporated, yielding brilliantly reflective, large, violet-red prismatic crystals from the concentrated solution. These are pressed dry on a clay plate and washed with alcohol and ether. A sample of this salt dried to constant weight at 100° gave the following analytic results: [116]

0.0628 g gave 0.0343 g $CoSO_4$

0.1010 g gave 0.0547 g $CoSO_4$

0.0778 g gave 10.2 ml Nitrogen at 14° and 723 mm pressure

0.1000 g gave 0.0973 g AgBr

0.1326 g gave 0.0196 g CO_2 and 0.0529 g H_2O

0.0820 g gave 0.0128 g CO_2 and 0.0345 g H_2O

	calc. for $Co_2N_6Br_3C_2O_4H_{23} \cdot 1H_2O$	found	
Co	20.66%	20.79%	20.61%
N	14.71	14.63	
Br	42.03	41.40	
C	4.21	4.03	4.25
H	4.37	4.43	4.79

The air-dried salt contains one more molecule of water than the above. This can be removed by heating at 110°.

0.1032 g gave 0.0537 g $CoSO_4$

	calc. for $Co_2N_6Br_3C_2O_4H_{23} \cdot 2H_2O$	found
Co	20.03%	19.98%

The salt dissolves easily in water, forming a light red solution. If some concentrated hydrobromic acid is added to this solution, a coalescent slurry of flake-like crystals forms which has a more brownish color than the original salt, but which consists of the same compound.

0.1479 g gave 0.0783 g $CoSO_4$

0.1382 g gave 18.4 ml Nitrogen at 20° and 724 mm pressure

0.1554 g gave 0.0239 g CO_2

0.1421 g gave 0.1373 g AgBr

	calc. for $Co_2N_6C_2O_4H_{23}Br_3$	found
Co	20.03%	20.14%
N	14.25	14.41
C	4.08	4.20
Br	40.80	41.12

When the bromide is covered with hydrochloric acid saturated at 0°, it dissolves to give a blue colored solution in which a rich precipitate of small crystals quickly forms. Only part of this product is soluble in water. The insoluble part consists of trichlorotriammine cobalt(III), $(H_3N)_3CoCl_3$, whose preparation from hexammine-tri-μ-hydroxo dicobalt(III) chloride has already been described.[1] [117]

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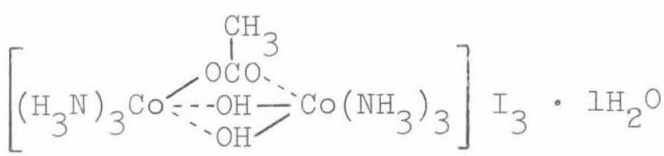
[1]Ber. d. d. chem. Ges. (1906) 39:2677

C. Iodide: 

If a solution of the bromide is treated with solid potassium iodide, or, better, if saturated potassium iodide solution is added dropwise to the solution, a strongly reflecting red salt crystallizes out in fine scales within a few moments. It is fairly insoluble in water and is therefore easily purified. The salt is sucked dry, washed with a little water and dried on a clay plate in a desiccator.

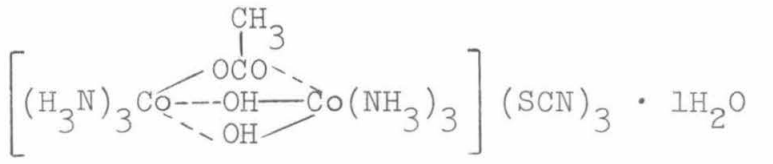
0.0837 g gave 0.0361 g $CoSO_4$

0.0946 g gave 0.0885 g AgI

0.1351 g gave 0.1282 g AgI

0.1836 g gave 13 ml Nitrogen at 20° and 714 mm pressure

	calc. for $Co_2N_6I_3C_2O_4H_{23} \cdot 1H_2O$	found	
Co	16.56%		16.41%
N	11.8		12.52
I	53.52	50.57	51.29

D. Thiocyanate: 

Enough potassium thiocyanate is added to a solution of the bromide to saturate it. The thiocyanate precipitates out as a fine red crystalline powder, which is sucked dry and purified by washing it with a little water. It is fairly soluble in water, forming solutions from which it can be reprecipitated by addition of potassium thiocyanate.

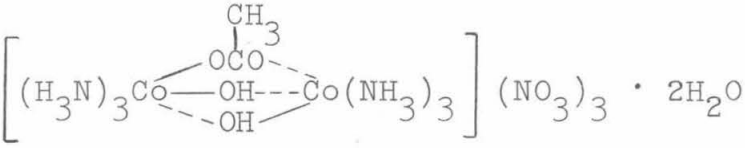
0.0960 g gave 0.0587 g $CoSO_4$

0.1148 g gave 27.5 ml Nitrogen at 17.5° and 715 mm pressure

0.1031 g gave 0.1482 g $BaSO_4$

0.1175 g gave 0.0544 g CO_2

	calc. for $Co_2N_9H_{23}C_5S_3O_4 \cdot 1H_2O$	found	[118]
Co	23.34%	23.26%	
N	24.95	27.19	
S	19.03	19.29	
C	11.87	12.63	

E. Nitrate: 

If a concentrated solution of hexammine-tri-μ-hydroxo dicobalt(III) nitrate to which glacial acetic acid has been added is evaporated to the point of crystallization, lustrous red intergrown monoclinic prismatic crystals up to 1 cm long can be obtained by slow cooling of the solution.

These crystals are freed of adhering mother liquor by placing them on a clay plate and washing them with alcohol and ether.

0.1025 g gave 0.0590 g $CoSO_4$

0.1388 g gave 0.0770 g $CoSO_4$

0.1000 g gave 21.0 ml Nitrogen at 16° and 722 mm pressure

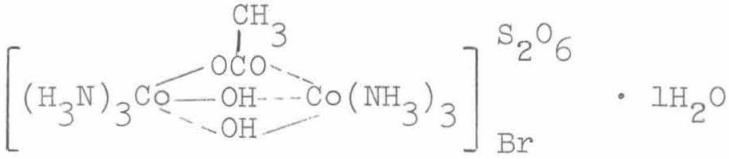
	calc. for $Co_2N_9C_2O_{13}H_{23} \cdot 2H_2O$	found	
Co	22.13%	21.91%	21.90%
N	23.63	23.20	

The salt loses 1 molecule of water on being heated at 100-110°. The analysis of the dried salt gave:

0.1000 g gave 0.0600 g $CoSO_4$

0.1000 g gave 22.0 ml Nitrogen at 16° and 724 mm

	calc. for $Co_2N_9C_2O_{13}H_{23} \cdot 1H_2O$	found
Co	22.90%	22.84%
N	24.46	24.38

F. Bromodithionate: 

A slight excess of solid sodium dithionate is added to a concentrated solution of diaquohexammine-di-μ-acetato dicobalt(III) bromide* and the mixture ground. A finely crystallized red salt

---

*Translator's note: This salt is not described elsewhere in this paper.

---

shortly precipitates and is removed by decanting as much of the solution as possible and pressing the salt free of the little remaining colored solution on a clay plate. It is then repeatedly ground into a thin slurry and the liquid removed with a clay plate. [119] The salt is finally dried in a desiccator.

0.1030 g gave 0.0549 g $CoSO_4$

0.1022 g gave 0.0543 g $CoSO_4$

0.1290 g gave 0.1007 g $BaSO_4$

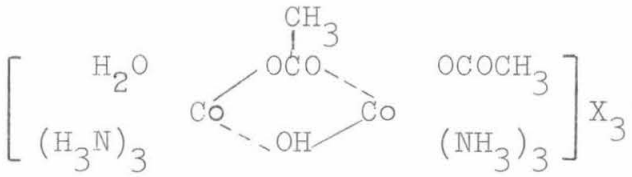
0.1214 g gave 15.7 ml Nitrogen at 19.5° and 719 mm pressure

0.1432 g gave 0.0242 g Co_2 and 0.0644 g H_2O

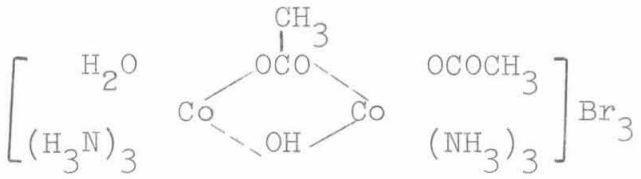
0.1055 g gave 0.0377 g AgBr

	calc. for $Co_2N_6C_2O_{10}H_{23}S_2Br \cdot 1H_2O$	found	
Co	20.63%	20.26%	20.21%
S	11.22	10.73	
N	14.72	14.28	
C	4.2	4.61	
H	4.41	5.03	
Br	14.00	15.21	

XXXI. Acetatoaquohexammine-μ-acetato-μ-hydroxo dicobalt(III) salts



A. Bromide:



If a saturated solution of hexammine-tri-μ-hydroxo dicobalt(III) bromide is treated with 1/2 its volume of glacial acetic acid, then is evaporated to 1/2 its volume in a water bath and subsequently cooled, red needles crystallize out which are then removed from the mother liquor and washed with alcohol and ether. After being dried in a desiccator over concentrated sulfuric acid the crystals appear dull, while if they are air-dried they retain their luster. Further evaporation of the mother liquor yields more of this salt. If the solution is concentrated too much, however, the color changes to blue at the temperature of the boiling water bath and on being [120]

being cooled, the solution yields a blue-red salt that crystallizes poorly and is different from the acetato-μ-acetato-μ-hydroxo salt.

Freshly prepared solutions of the cetato-μ-acetato-μ-hydroxo salt are acidic; the salt must consequently be an aquo salt.

The salt dried in a desiccator gives the following analytical results:

0.0935 g gave 0.0455 g $CoSO_4$

0.1023 g gave 0.0910 g AgBr

0.1324 g gave 16.0 ml Nitrogen at 20° and 732 mm pressure

0.1498 g gave 0.0395 g Co_2 and 0.0707 g H_2O

	calc. for $Co_2N_6C_4O_6H_{27}Br_3$	found
Co	18.69%	18.51%
N	13.34	13.56
Br	38.00	37.85
C	7.60	7.19
H	4.63	5.28

This salt is very unstable in aqueous solution since only salts of the hexammine-μ-acetato-di-μ-hydroxo dicobalt(III) series are obtained from such solutions when the precipitation is caused by addition of various salts.

The acetato-μ-acetato-μ-hydroxo dicobalt(III) bromide can also be obtained from hexammine-μ-acetato-di-μ-hydroxo dicobalt(III) bromide.

A concentrated solution of this bromide is treated with an equal volume of glacial acetic acid and evaporated until the heat

causes a light crystalline skin to form on the surface of the solution. On cooling, the salt precipitates out as fine crystalline needles, which are filtered off, washed with ether, pressed out on a clay plate and dried.

0.1048 g gave 0.0515 g $CoSO_4$

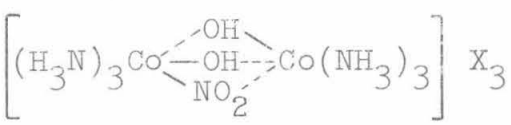
0.1092 g gave 0.0964 g AgBr

	calc. for $Co_2N_6C_4O_6H_{27}Br_3$	found
Co	18.69%	18.69%
Br	38.00	37.57

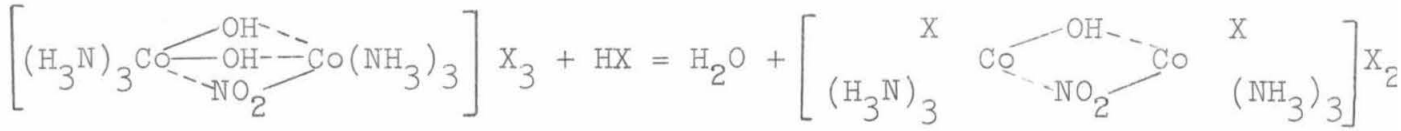
It is to be noted that frequently salts are obtained in these preparations that contain too little carbon, probably because a mixture of monoacetato and diacetato salts is easily formed.

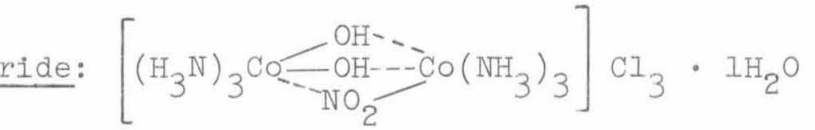
XXXII. Hexammine-μ-nitrito-di-μ-hydroxo dicobalt(III) salts [121]

by A. Grün and E. Bindschedler



Salts of this series are formed by the reaction of nitrous acid with the hexammine-tri-μ-hydroxo dicobalt(III) salts in weak aqueous acetic acid solution. The salts have a deep orange color and are distinguished by the extraordinarily strong bonding of the nitrito group. By boiling their solutions with hydrochloric acid or hydrobromic acid one hydroxyl bridge is cleaved and two halogen atoms enter the complex radical, but no nitrous acid is liberated.



A. Chloride: 

Ten grams of hexammine-tri-μ-hydroxo dicobalt(III) chloride are dissolved in 50 ml of water containing some acetic acid and the filtered solution is treated with 2 g of $NaNO_2$ (corresponding to 1 mole). This is stirred until all of the nitrite has dissolved. The now orange colored solution is heated at 40-50° and then treated with about 30 ml of concentrated hydrochloric acid. The new chloride immediately begins to precipitate and a thick crystal slurry forms quickly while the color of the solution fades to a weak reddish-violet. The orange-colored salt is sucked dry, washed with half-strength HCl until the filtrate is colorless, and is then washed free of acid with alcohol. (Yield: 8.5 grams.) The 8.5 grams are dissolved in 110 ml of water and the filtered cooled solution is treated with 100 ml of concentrated HCl. The pure chloride precipitates as lustrous matted needles. (Yield: 7 grams.)

The analysis of the air-dried salt gave: [122]

0.1050 g gave 0.0770 g $CoSO_4$

0.1043 g gave 0.0754 g $CoSO_4$

0.1004 g gave 20.8 ml Nitrogen at 13° and 723 mm pressure

0.1068 g gave 22.4 ml Nitrogen at 16° and 723 mm pressure

0.1157 g gave 0.1146 g AgCl

0.1026 g gave 0.1014 g AgCl

	calc. for $Co_2N_7O_4H_{20}Cl_3 \cdot H_2O$	found
Co	27.91%	27.52%
N	23.23	23.20
Cl	24.50	24.44

The chloride is obtained in a very beautifully crystallized from in the following way. Four gram of the salt are dissolved in 20 ml of water by the addition of some acetic acid and heat, and the solution is allowed to cool slowly in the same water bath that was used for the warming of the solution. As can be seen under a microscope the crystals formed occur as long, radially intergrown, lustrous, orange-red rods.

B. Bromide: $\left[(H_3N)_3Co\begin{matrix}OH \\ OH \\ NO_2\end{matrix}Co(NH_3)_3\right]Br_3 \cdot 1H_2O$

A lukewarm solution of hexammine-tri-μ-hydroxo dicobalt(III) bromide was acidified with acetic acid and then treated with an excess of sodium nitrite. After about 10 minutes of frequent stirring, the solution turned orange-red. By dropwise addition of hydrobromic acid, which caused the evolution of nitrous oxides, and intensively orange-red, finely crystallized precipitate of the bromide was obtained. After being sucked dry, redissolved in water and reprecipitated by addition of hydrobromic acid, the pure bromide crystallizes as orange-red, lustrous matted flakes. It is difficultly soluble in water. Samples of this salt dried at 100° gave the following analytical results:

0.1116 g gave 0.0607 g $CoSO_4$

0.1100 g gave 0.0600 g $CoSO_4$

0.2024 g gave 0.2050 g AgBr

0.2006 g gave 0.2056 g AgBr

0.1169 g gave 19.4 ml Nitrogen at 17° and 721 mm pressure

0.1013 g gave 16.1 ml Nitrogen at 15° and 715 mm pressure

0.1462 g gave 23.8 ml Nitrogen at 16° and 714 mm pressure

0.1790 g gave 29.3 ml Nitrogen at 14° and 704 mm pressure

	calc. for $Co_2N_7O_4H_{20}Br_3 \cdot 1H_2O$	found			[123]
Co	21.14%		20.69%	20.75%	
N	17.56	18.22	17.46	17.79	17.77
Br	43.01		43.09	43.50	

C. Nitrate: $\left[(H_3N)_3Co\begin{smallmatrix}OH\\OH\\NO_2\end{smallmatrix}Co(NH_3)_3\right](NO_3)_3 \cdot H_2O$

The nitrate is prepared by treating an aqueous solution of the chloride with nitric acid. It precipitates as micaceous flakes which are purified by reprecipitation.

Four grams of chloride are dissolved in 50 ml of water and 50 ml of nitric acid are added, without stirring, to the solution which is simultaneously strongly cooled. Crystallization begins as soon as the first drop of nitric acid has been added. The solution remains colored, but on standing for a long time with concentrated nitric acid the color changes from orange to violet. The mixture is suction filtered and the precipitate washed with half strength nitric acid. The salt is then washed free of acid

with alcohol to yield, on being dried in the air, 2.5 g of salt which may be further purified by recrystallization. It is much more insoluble than the chloride. 2.5 g can dissolve in 60 ml of water; if 40 ml of concentrated nitric acid is carefully added to such a solution, the salt forms brightly reflective rhombohedral plates that are somewhat more reddish than the chloride. (Yield 2 grams.)

0.1056 g air dried salt gave 0.0650 g $CoSO_4$

0.1022 g gave 25.8 ml Nitrogen at 16° and 720 mm pressure

	calc. for $Co_2N_{10}O_{13}H_{20} \cdot H_2O$	found
Co	23.41%	23.42%
N	27.77	27.81

D. <u>Sulfate</u>: $\left[(H_3N)_3Co\begin{matrix}OH\\OH\\NO_2\end{matrix}Co(NH_3)_3\right]_2(SO_4)_3 \cdot 2H_2O$

Four grams of $Na_2SO_4 \cdot 10\ H_2O$ are slowly added to a filtered solution of 4 g of chloride in 50 ml of water. A thick slurry of crystals froms as soon as the former has dissolved. Another 4 g of sodium sulfate are added and the resulting orange-red crystalline salt is removed by suction filtration and washed with cold water, [124] in which it is almost insoluble. The filtrate is only weakly pink colored. (Yield: 3.4 grams.)

This sulfate is dissolved in 800 ml of weak aqueous acetic acid solution in a dish by being heated to boiling. The resulting solution is quickly filtered. The sulfate crystallizes out in

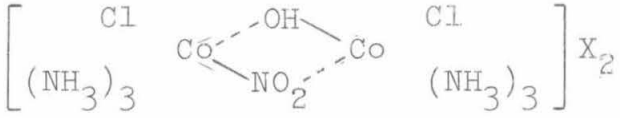
rhombohedral, many sided prisms as the solution cools, while the mother liquor remains strongly colored because only about 1.8 g is thus precipitated. The remainder can be obtained by evaporating the mother liquor.

0.1086 g air dried salt gave 0.0726 g $CoSO_4$

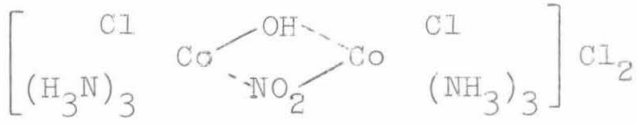
0.1036 g gave 20.0 ml Nitrogen at 17° and 720 mm pressure

	calc. for $Co_4N_{14}S_8O_{22}H_{44}$	found
Co	25.54%	25.44%
N	21.21	21.16

XXXIII. Dichlorohexammine-μ-nitrito-μ-hydroxo dicobalt(III) salts



by E. Bindschedler and E. Welti

A. Chloride: 

Hexammine-μ-nitrito-di-μ-hydroxo dicobalt(III) chloride is not affected by cold concentrated hydrochloric acid; when a mixture of the two is heated, however, the color changes to violet and a dark violet finely crystalline salt is obtained. This salt is difficulty soluble in water and may be reprecipitated from such solutions by addition of hydrochloric acid or ammonium chloride.

This compounds is prepared as follows: 6 grams of hexammine-μ-nitrito-di-μ-hydroxo dicobalt(III) chloride are ground with 36 ml

of hydrochloric acid solution (27 ml conc. HCl and 9 ml water) in a beaker and heated in a water bath. The reaction begins immediately and is easily followed by observing the changes in color. The [125] orange-red salt at first changes to brown, then red-brown, and finally to violet.

As soon as the color has changed to violet, the heat is removed and the solution allowed to cool. The salt is then suction-filtered from the solution and washed free of acid with alcohol and ether. Yield: 4.5 grams. The salt is difficulty soluble in cold water. If it is heated with water, the initially violet solution changes color to orange-red and on addition of hydrochloric acid hexammine-μ-nitrito-di-μ-hydroxo dicobalt(III) chloride precipitates from it.

In order to purify the chloride, one proceeds as follows: 4.5 g of crude chloride are dissolved in 210 ml of cold water and the filtered, strongly cooled violet solution is treated with 150 ml of concentrated hydrochloric acid, precipitating the salt as very fine crystals. After a few hours the salt is suction filtered from the solution and washed, first with half-strength hydrochloric acid and then acid-free with alcohol and ether. Yield: 3.5 grams of violet plate-like crystals with lustrous faces.

0.1000 g gave 0.0730 g $CoSO_4$
0.0930 g gave 0.0678 g $CoSO_4$
0.1036 g gave 0.0752 g $CoSO_4$
0.1174 g gave 0.0852 g $CoSO_4$
0.1022 g gave 21.4 ml Nitrogen at 16° and 720 mm pressure
0.1000 g gave 19.6 ml Nitrogen at 10° and 732 mm pressure

0.1072 g gave 21.7 ml Nitrogen at 15.5° and 727 mm pressure

0.1009 g gave 20.4 ml Nitrogen at 16° and 728 mm pressure

0.1006 g gave 0.1342 g AgCl

0.1035 g gave 0.1367 g AgCl

	calc. for $Co_2N_7O_3Cl_4H_{19}$	found			
Co	27.76%	27.78%	27.75%	27.63%	27.63%
N	23.07	23.07	22.56	22.57	22.52
Cl	33.36		33.00	32.67	

Welti's analyses:

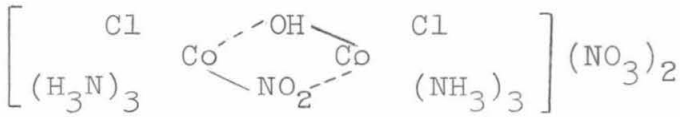
0.0977 g gave 0.0705 g $CoSO_4$

0.1214 g gave 25.2 ml Nitrogen at 21° and 728 mm pressure

0.0988 g gave 0.1331 g AgCl

0.0968 g gave 0.1294 g AgCl

	found	
Co	27.45%	
N	23.09	
Cl	33.31	33.05

B. <u>Nitrate</u>:  [126]

The nitrate has been prepared by two methods.

First method: 3 g of violet chloride are dissolved in 150 ml of water and the then strongly cooled filtered solution treated with 100 ml of concentrated nitric acid. The nitrate precipitates

almost instantaneously as dark violet crystals. In spite of this, the solution remains strongly colored but no significant additional amount of the nitrate precipitates even after the solution has been allowed to stand for several days. (Yield: 2 grams.)

The salt prepared in this way (Analysis I) is a flaky crystalline powder that has a somewhat deeper violet color than the chloride. Only 0.2 g of salt will dissolve in 150 ml of water.

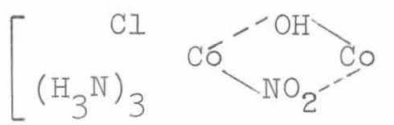
Second method: The chloride is triturated with a saturated solution of sodium nitrate and the product thus obtained is treated again this way after it has been separated from the liquor. The salt is freed of adhering sodium nitrate by grinding it in a little water and spreading it out on a clay plate.

The salt decomposes completey when heated to 100° but no weight is lost at lower temperatures.

I. 0.1022 g gave 0.0676 g $CoSO_4$
0.1000 g gave 24.6 ml Nitrogen at 16° and 710 mm pressure
0.1512 g gave 0.0028 g AgCl

II. (2 different preparations following method 2)
0.0955 g gave 0.0631 g $CoSO_4$
0.1012 g gave 0.0644 g $CoSO_4$
0.1023 g gave 0.0623 g AgCl
0.1103 g gave 0.0668 g AgCl
0.0961 g gave 23.4 ml Nitrogen at 21° and 722 mm pressure
0.1330 g gave 32.3 ml Nitrogen at 21.5° and 729 mm pressure

	calc. for $Co_2N_9Cl_2O_9H_{13}$	found I	found II	
Co	25.20%	25.17%	25.14%	24.96%
N	26.65	26.60	26.86	27.05
Cl	15.00	14.35	14.91	14.97

C. Sulfate:  [127]

The chloride is pulverized with a saturated solution of sodium sulfate on a watch glass. The reaction occurs immediately as is easily observable since a much more voluminous precipitate of violet salt is formed which takes on a slurry-like consistency. The product is pressed dry on a clay plate, again ground with concentrated sodium sulfate solution, suction filtered and freed of adhering sodium sulfate by repeated trituration with water. The yield is nearly quantitative, as the sulfate is significantly less soluble than the chloride.

0.0781 g gave 0.0519 g $CoSO_4$

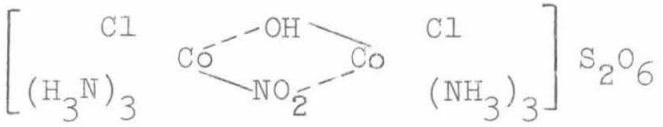
0.0956 g gave 18.10 ml Nitrogen at 18° and 720 mm pressure

0.0828 g gave 0.0500 g AgCl

0.0828 g gave 0.0427 g $BaSO_4$

	calc. for $Co_2N_7O_7Cl_2H_{19}S \cdot 1H_2O$	found
Co	25.21%	25.28%
N	20.95	21.04
Cl	15.14	15.28
S	6.85	7.08

The determination of the water of hydration by heating in a drying oven was unsuccessful because the salt decomposed near 100°; continuous heating at lower temperatures did not give any weight loss.

D. Dithionate:  S_2O_6

The dithionate is prepared by triturating the chloride with a concentrated solution of sodium dithionate, using a procedure similar to that used to make the sulfate. The dithionate is very difficultly soluble in water and forms a powder of small violet crystals.

0.0974 g gave 0.0574 g $CoSO_4$

0.0898 g gave 0.0502 g AgCl

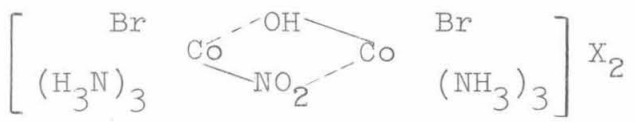
0.0898 g gave 0.0832 g $BaSO_4$

0.1017 g gave 17.6 ml Nitrogen at 18° and 725 mm pressure

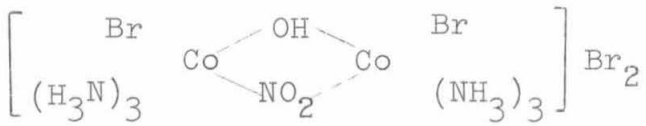
	calc. for $Co_2N_7O_9Cl_2H_{19}S_2$	found
Co	22.94%	22.42%
Cl	13.79	13.82
S	12.49	12.72
N	19.07	19.37

[128]

XXXIV. Dibromohexammine-μ-nitrito-μ-hydroxo dicobalt(III) salts

 X_2

by E. Welti

A. Bromide: 

About 1/2 gram of μ-nitrito-di-μ-hydroxo bromide is covered with concentrated hydrobromic acid so as to form a paste. By careful heating of the mixture over a small flame the orange salt is transformed into a grey-black salt. After being cooled, the pale green supernatant is poured off and the slurry of small crystals placed on a clay plate. In order to remove the remaining hydrobromic acid and some μ-nitrito-di-μ-hydroxo salt still present, the reaction product is again made into a paste once or twice with cold water, each time being pressed out on a clay plate, and is finally dried in a desiccator.

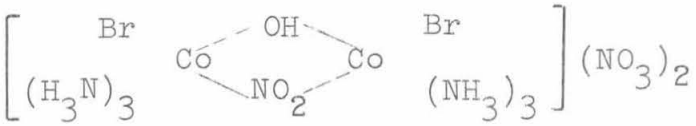
The bromide forms a grey-black finely crystallized powder that is somewhat soluble in water. It forms blue-violet solutions. Its solutions are unstable to heating, quickly taking on an orange-red color.

0.1204 g gave 0.0664 g $CoSO_4$

0.0981 g gave 0.1216 g AgBr

0.1318 g gave 18.9 ml Nitrogen at 22° and 728 mm pressure

	calc. for $Co_2N_7O_3H_{19}Br_4$	found
Co	19.57%	19.40%
N	16.26	15.90
Br	53.04	52.75

B. Nitrate:  [129]

One-half gram of bromide is added to a saturated solution of sodium nitrate containing some excess solid sodium nitrate, and the mixture ground for several minutes. After the salt has settled, the clear, only weakly violet colored solution is poured off. The whole operation is repeated and the resulting salt is then twice ground into a paste with a little water and pressed out on a clay plate to remove any excess sodium nitrate.

The nitrate also is a violet to grey-black powder which is somewhat more soluble in water than the bromide. Its solutions are blue-violet, but change to orange-red after a short time.

Desiccator-dried salt was used in the analysis.

0.0823 g gave 0.0452 g $CoSO_4$

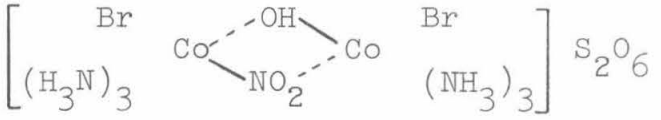
0.0989 g gave 0.0539 g $CoSO_4$

0.1029 g gave 0.0675 g AgBr

0.1316 g gave 0.0864 g AgBr

0.0942 g gave 18.9 ml Nitrogen at 21° and 710 mm pressure

	calc. for $Co_2N_0{}^0{}_9H_{19}Br_2$	found	
Co	20.81%	20.89%	20.73%
N	22.23	21.76	---
Br	28.19	27.92	27.94

C. Dithionate: 

The dithionate was prepared in a way similar to that of the nitrate, namely by triturating the solid bromide with a saturated solution of sodium dithionate and extracting the reaction product twice with a little water. The dithionate is slightly more grey-colored than the bromide and is only slightly soluble in water.

0.0749 g gave 0.0382 g $CoSO_4$

0.0863 g gave 0.0439 g $CoSO_4$

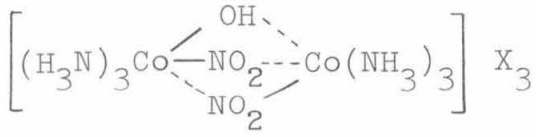
0.1153 g gave 0.0718 g AgBr

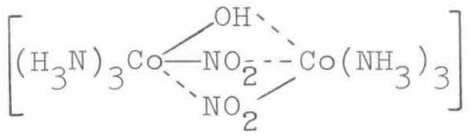
0.1153 g gave 0.0928 g $BaSO_4$

	calc. for $Co_2N_7O_9H_{19}Br_2S_2$	found	
Co	19.57%	19.40%	19.35%
Br	26.49	24.50	
S	10.63	11.05	

[130]

XXXV. Hexammine-di-μ-nitrito-μ-hydroxo dicobalt(III) salts



A. Chloride: 

On the basis of numerous attempts to prepare this salt the following procedure has proved to be the most suitable.

0.5 g of dichlorohexammine-μ-nitrito-μ-hydroxo dicobalt(III) chloride, 0.8 g of $NaNO_2$, 10 ml of water, and 2 ml of acetic acid are heated over an open flame until an orange solution has formed. Concentrated nitric acid is then added and the salt is allowed to crystallize, red-orange needles being formed after a while.

1.3 g of nitrate were obtained from 10 portions (5 g). Since the salt contains traces of the mononitrito compound, it is converted into pure chloride in the following manner.

1.3 g are dissolved in 50 ml of half-strength hydrochloric acid with heating and the resulting solution is poured as quickly as possible through a fluted filter. Magnificent orange colored needles (0.65 g) crystallize out of the beautifully orange-colored solution after a short time. The still strongly colored mother liquor yields another 0.5 g on standing for a longer period in a desiccator.

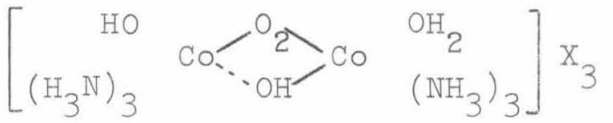
0.1074 g air dried salt lost 0.0038 g in a desiccator over H_2SO_4
Heating at 100° led to a weight loss of 5.58%, but traces of decomposition were observed.

0.1074 g gave 0.0751 g $CoSO_4$
0.1030 g gave 23.0 ml Nitrogen at 10° and 717 mm pressure
0.1006 g gave 0.0953 g AgCl

	calc. for $Co_2N_8O_5H_{19}Cl_3 \cdot \frac{1}{2}H_2O$	found
Co	26.40%	26.61%
N	25.30	25.17
Cl	23.80	23.40

[131]

XXXVI. Hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) salts



This series is obtained if the preparation of Melano chloride is carried out at temperatures below 5°. On the basis of our extensive experiments, we recommend the following method. About 50 g of cobalt(II) chloride, $CoCl_2 \cdot 6H_2O$, are dissolved in 30 ml of water with heating and 275 ml of concentrated ammonia (specific gravity = 0.917) are added. The mixture is quickly heated to boiling, the precipitated cobalt oxide is filtered off and the solution allowed to stand in a dish for five or six days at near zero temperature. The red crystalline crust is then filtered off, and 175 ml of concentrated hydrochloric acid are added to the red-brown solution. After about 10 minutes and the evolution of a great deal of chlorine, a brown salt mixture precipitates out which is then separated from the liquor and extracted with water until the residue has a pure grey color. The mother liquor, containing hydrochloric acid, yields another black salt mixture, from which some more Melanochloride may be extracted. The yield of grey Melano salt is about 65 g per kilogram of cobalt chloride.

A. Processing of the Melanochloride

Melano chloride that has been well dried can be very conveniently processed according to the following method.

About 20 g of Melano salt are covered with a solution of 38.5 g of silver nitrate in 60 ml of water weakly acidified with HNO_3, and the mixture is ground. The mass becomes quite warm in the course of the reaction and it is therefore advantageous [132] to cool the mixture somewhat from the beginning. After the primary reaction is complete, the mixture is heated with stirring to 50° and the resulting dark brown solution is drawn off (Solution I). The silver chloride precipitate is then heated in 60 ml of water to 80° and the solution again drawn off (Solution II). The silver chloride residues from a large number of such preparations are combined and twice extracted with the corresponding amount of weak nitric acid solution at 80° (Solutions III and IV).

A nearly black salt precipitated almost immediately from Solution I after it had been drawn off. After a while a red salt precipitated with the black. Solution II behaved similarly on standing for a while. From Solutions III and IV only red salt precipitated on standing. After standing at near-zero temperature for six hours, all the precipitated salts were removed from their mother liquor. The total yield from 517 g Melanochloride was 430 g of nitrate mixture.

B. Processing of the nitrate mixture

In order to isolate the new series from the nitrate just obtained the following method was used. 50 g portions of the mixture were triturated twice with 100 ml of cold water and the resulting brown solutions were decanted off. Finally the

304 g still remaining out of the original 430 g were extracted in portions of about 100 g with 100 ml of water each. A 280 g portion of nitrate having a dark brown-red color remained undissolved; its further processing will be described later. The collected brown solutions were then ground with excess ammonium bromide, whereupon each mixture solidified into brownish-green slurries of needle-like crystals which were then separated from the now red liquors. The liquors, on standing for a longer period, yield yet other, different salts that will not be considered here. The brownish-green bromide (99 g) obtained in [133] the described manner was dissolved in portions of about 5 g each in 20 ml aliquots of weak aqueous acetic acid in a hot water bath and the warm solutions were treated with ammonium sulfate. A dark green sulfate immediately precipitated out that was removed from the green mother liquor. More of the green sulfate was recovered by completely saturating the mother liquors with ammonium sulfate and allowing them to stand. These can be transformed into dichlorohexammine-μ-amido-μ-peroxo dicobalt(III,IV) chloride by heating with some hydrochloric acid; 10 g of this salt was obtained in this way. The amount of directly precipitated sulfate was 78 g. Portions of about 15 g of this were heated for a short time with 30 ml of water containing acetic acid in a water bath, the resulting solutions were decanted, and the residues digested three times with about 45 ml of weak acetic acid solution in a water bath. While the first aqueous extract was green and the last one possessed a pure brown color,

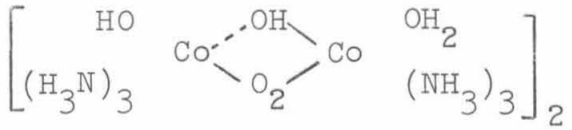
those in between showed a mixture of colors. A brown salt in the form of lustrous flakes is obtained as undissolved residue, this being the sulfate of the new series. 32 g of this salt were prepared in this way. The liquors yielded for insoluble chloro compounds when treated with concentrated hydrochloric acid.

The 230 g of undissolved residue mentioned above were processed in the following way:

Portions of about 100 g were covered with 200 ml of water and after about 20 minutes suction filtered. 50 g of ammonium sulfate were added to the clear solution and, after the greater part of this had dissolved, 100 ml of glacial acetic acid were added, giving a black ammonium double sulfate which began to precipitate after a short time. The undissolved residues contained a great deal of black salt and were therefore extracted with water three times in the same way. The black salt could also be precipitated from these solutions by adding 50 g of [134] ammonium sulfate and 100 ml of glacial acetic acid for each 200 ml of solution. 175 g of black ammonium double sulfate were obtained from the 280 g, and 65 g of red Melano nitrate remained behind.

The ammonium double sulfate is quite soluble in cold water. If a concentrated solution containing acetic acid is heated to boiling, the normal, slightly soluble sulfate of the new series precipitates out on cooling, thus allowing good purification and isolation of the new series of salts.

The two sulfates served as the starting material in the preparation of the salts described below.

C. Sulfate: 

The sulfate is a magnificently crystallized salt. It consists of black, often fairly large, glassy, brown crystalline flakes. It shows a brown tone when ground. It is only slightly soluble in water, forming a basic solution. It is more soluble in aqueous acetic acid solution and can be recrystallized from hot solutions containing a little acetic acid.

0.1022 g gave 0.0704 g $CoSO_4$

0.0913 g gave 0.0630 g $CoSO_4$

	calc. for $[Co_2N_5O_5H_{22}]_2(SO_4)_3$	found	
Co	26.39%	26.21%	26.26%

D. Quantitative determination of the nitrogen and oxygen liberated in the decomposition with concentrated sulfuric acid

These determinations were carried out according to the method described for octammine-μ-amido-μ-peroxo dicobalt(III,IV) sulfate.

I. 0.1001 g gave 5.2 ml Oxygen and 1.5 ml Nitrogen at 18.5° and 727.5 mm, corresponding to 6.51% Oxygen and 1.64% Nitrogen.

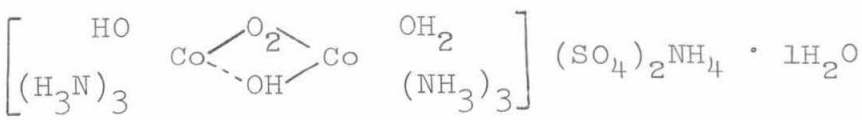
II. 0.1017 g gave 5.5 ml Oxygen and 1.5 ml Nitrogen at 19° and 727 mm, corresponding to 6.75% Oxygen and 1.61% Nitrogen.

III. 0.1040 g gave 5.6 ml Oxygen and 1.4 ml Nitrogen at 17° and 731 mm, corresponding to 6.83% Oxygen and 1.49% Nitrogen.

Theoretically, the amount of nitrogen, assuming two valences, should be 2.07%, and the amount of oxygen, with three valences should be 5.3%. [135]

There is thus too little nitrogen and too much oxygen. If the amount of oxygen corresponding to the five valences is calculated, then theoretically 8.9% of oxygen is required. 7.0% is required for four valences and 10.6% for six valences. The experimental amount of nitrogen and oxygen corresponds to the following amounts of oxygen: I. 9.2%; II. 9.4%; III. 9.3%, i.e., values which agree only with the value calculated for five valences. That the amount of oxygen is slightly too great is due to the method that was used, since it is well known that ordinary nitrogen gas determinations frequently gives somewhat high values.

E. Ammonium sulfate double salt:



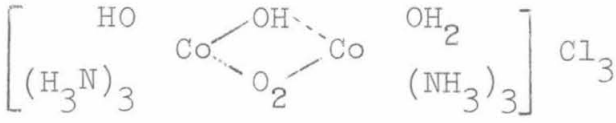
This salt is prepared by dissolving hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) nitrate in a little water, saturating the clear solution with ammonium sulfate and then adding an equal volume of glacial acetic acid. The double salt crystallizes out in black crystals after a short time.

0.1411 g gave 0.0822 g $CoSO_4$

0.1395 g gave 0.1214 g $BaSO_4$

	calc.	found
Co	22.14%	22.16%
S	12.00	11.95

The salt is quite soluble in water. If a solution containing acetic acid is heated to boiling, the very difficultly soluble sulfate of the hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) series precipitates out on cooling.

F. Chloride:  [136]

One g of sulfate is covered with a little weak acetic acid solution and ground with an excess of ammonium chloride. The resulting mixture loses its crystallinity and turns bright brown. The reaction product is filtered off, dissolved in a little water and reprecipitated with ammonium chloride. It is then redissolved in a little weak acetic acid solution with light heating and some alcohol is added. On cooling, the chloride crystallizes out as brown lustrous needles.

0.1002 g gave 0.0763 g $CoSO_4$

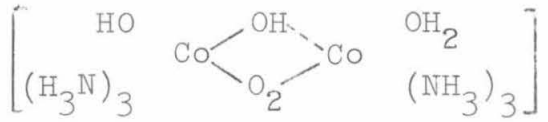
0.1028 g gave 19.5 ml Nitrogen at 19° and 723 mm pressure

0.1030 g gave 19.6 ml Nitrogen at 19° and 720 mm pressure

0.1093 g gave 0.1147 g AgCl

	calc. for $Co_2N_5O_5H_{22}Cl_3$	found	
Co	28.82%	28.93%	
N	20.52	20.62	20.58
Cl	25.97	25.89	

The chloride is quite soluble in water, forming brown solutions.

G. Bromide: 

The sulfate is easily converted into the bromide by grinding it with an excess of ammonium bromide in a little water. The product is dissolved in a little water and reprecipitated with ammonium bromide. Well formed, needle-like, greenish brown crystals result when the crystallization is carried out from a warm, weak acetic acid solution by the addition of a little alcohol.

0.1008 g gave 0.0555 g $CoSO_4$

0.1025 g gave 0.0571 g $CoSO_4$

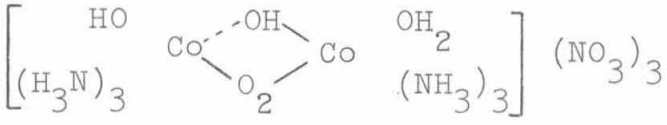
0.1039 g gave 14.3 ml Nitrogen at 18° and 723 mm pressure

0.1057 g gave 0.1062 g AgBr

	calc. for $Co_2N_6O_5H_{22}Br_3 \cdot 1H_2O$	found		[137]
Co	21.03%	20.95%	21.12%	
N	14.97	15.04		
Br	42.78	42.75		

The bromide is easily dissolved in water to give a brown, weakly basic solution. The solid bromide changes color on

standing, becoming more reddish. Whether or not this is a reduction reaction has not been established.

H. Nitrate: 

One g of sulfate is ground with a little dilute acetic acid and ammonium nitrate and the nitrate filtered out, redissolved in water, and reprecipitated with ammonium nitrate. Glassy, black-brown, plate-like crystals are obtained by recrystallizing the nitrate from a little warm water by adding small amounts of alcohol. Rubbing the crystals gives a pure brown streak.

0.1010 g gave 0.0648 g $CoSO_4$

0.1003 g gave 0.0646 g $CoSO_4$

0.1015 g gave 23.9 ml Nitrogen at 19.5° and 727 mm pressure

0.0963 g gave 22.2 ml Nitrogen at 16° and 731 mm pressure

	calc. for $Co_2N_9O_{14}H_{22}$	found	
Co	24.13%	24.41%	24.43%
N	25.76	25.66	25.71

The nitrate dissolves easily in water forming a brown, alkaline solution.

XXXVII. Chlorodiaquopentammine-μ-amido-μ-peroxo dicobalt(III,IV) salts*

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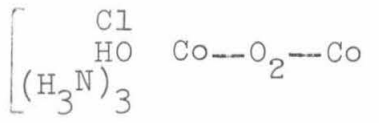
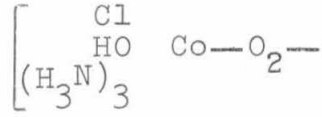
*Translator's note: This heading is inconsistent with the contents of this section. Werner probably means trichlorohydroxo hexammine-μ-peroxo dicobalt(III,IV) salts.



A. Chloride: 

If the nitrate just described is dissolved in a cold aqueous acetic acid solution, treated with some concentrated sulfuric acid and the solution allowed to stand for a short period, small grey-black crystals form that have a greasy luster. The precipitation can be speeded up by heating the solution slightly, the salt being formed almost instantaneously. The chloride can be prepared from the sulfate. A solution of 2 g of sulfate in 5 ml of concentrated hydrochloric acid is quickly heated to the point of boiling and the solution immediately cooled. Gas is vigorously evolved and the chloride settles out as a grey-black salt while the liquid shows occurrence of partial decomposition since it turns blue. [138]

0.1031 g gave 0.0774 g $CoSO_4$

0.0944 g gave 0.0704 g $CoSO_4$

0.1504 g gave 0.2093 g AgCl

0.1694 g gave 32.2 ml Nitrogen at 18° and 726 mm pressure

	calc. for $Co_2N_6O_3H_{19}Cl_4$	found	
Co	28.60%	28.48%	28.29%
N	20.48	20.95	
Cl	34.40	34.41	

B. Nitrate: $\left[\begin{matrix} Cl \\ HO \\ (H_3N)_3 \end{matrix} Co—O_2--Co \begin{matrix} Cl_2 \\ (NH_3)_3 \end{matrix}\right] NO_3$

The chloride is used as the starting material in the preparation of this salt. It is ground thoroughly with concentrated nitric acid and then pressed out on a clay plate. This is repeated twice and the resulting salt washed with alcohol and ether. The nitrate used in the analysis was dried in a desiccator over sulfuric acid.

0.1523 g gave 0.1062 g $CoSO_4$

0.1488 g gave 0.1473 g AgCl

	calc. for $Co_2N_7H_{19}O_6Cl_3$	found
Co	26.90%	26.70%
Cl	24.30	24.42

C. Effect of liquid ammonia on the chloride

If the chloride just described is covered with liquid ammonia in a large reaction tube, it dissolves to give a brown solution which in turn gives a yellow-red residue after evaporation of [139] the ammonia. This product is quite soluble water. By adding hydrobromic acid to an aqueous solution of this residue a yellow precipitate is formed, which on crystallization from dilute hydrobromic acid gives pure hexammine cobalt(III) bromide.

0.1500 g gave 0.0591 g $CoSO_4$

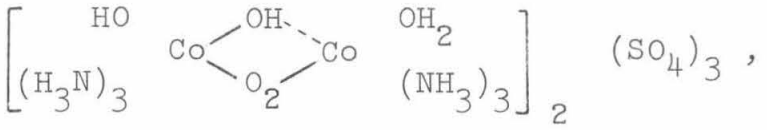
0.1570 g gave 31.1 ml Nitrogen at 17° and 718 mm pressure

	calc. for $CoN_6H_{18}Br_3$	found
Co	14.75%	14.99%
N	21.00	21.55

Bromopentammine cobalt(III) bromide is precipitated when the hydrobromic acid containing mother liquor is heated. It is apparent from this product that the two cobalt atoms of the black series cannot be bound together with an amido bridge, since such a bridge is not cleaved by liquid ammonia.

D. Reduction of the hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) series

Ten g of hydroxoaquohexammine-μ-peroxo-μ-hydroxo dicobalt(III,IV) sulfate,



were covered with 15 ml of water and 20 ml of glacial acetic acid, and 5 g of sodium iodide was added to the mixture. Amid the vigorous evolution of a gas, a brown solution was formed to which another 5 g of sodium iodide were added. The solution solidified to a brown crystalline slurry on being heated which took on a pale red color on the addition of 10 ml of water and 10 g of sodium thiosulfate. The crystalline precipitate, after being filtered off, was ground with a little water and ammonium bromide and the resulting bromide was then filtered off and reprecipitated twice from a concentrated aqueous

solution using ammonium bromide. Lustrous, bluish-red flakes are thus obtained which dissolve quite easily in water to give a light red solution. Most of the salt remained in the liquor during reprecipitation, thus giving a yield of only 3.5 g of doubly reprecipitated bromide. [140]

0.1005 g gave 0.0530 g $CoSO_4$

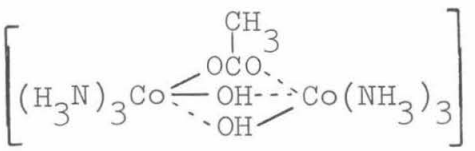
0.1111 g gave 14.5 ml Nitrogen at 19° and 724 mm pressure

0.1018 g gave 0.0969 g AgBr

0.1020 g gave 0.0150 g CO_2 and 0.0459 g H_2O

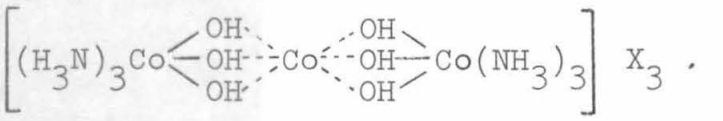
	calc. for $Co_2N_6O_4H_{23}Br_3 \cdot 2H_2O$	found
Co	20.03%	20.00%
N	14.26	14.21
C	4.07	4.00
H	4.92	5.00
Br	40.74	40.50

Both the analysis and the chemical behavior have shown that the reaction product thus obtained is identical to that prepared from hexammine-tri-μ-hydroxo dicobalt(III) bromide by reaction with acetic acid, namely, <u>hexammine-μ-acetato-di-μ-hydroxo dicobalt(III) bromide</u>:



The bromide is recovered unaltered by reprecipitation from concentrated aqueous solution with hydrobromic acid. Trichlorotriamine cobalt(III), $[Cl_3Co(NH_3)_3]$, results from reaction of the salt with fuming hydrochloric acid.

XXXVIII. Hexammine-hexa-μ-hydroxo tricobalt(III) salts



In the preparation of hexammine-tri-μ-hydroxo dicobalt(III) sulfate from chlorodiaquotriammine cobalt(III) sulfate[1] a deep red-brown

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[1]Ber. d. d. chem. Ges. (1907) 40:4837

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concentrated mother liquor is obtained in addition to the precipitate of red sulfate. This mother liquor contains a number of salts, one of which may be relatively easily isolated by the following method.

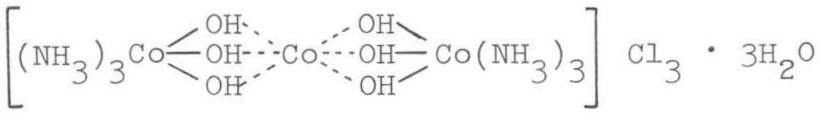
The liquor resulting from the processing of 15 g of chlorodiaquotriammine cobalt(III) sulfate (7 g of hexammine-tri-μ-hydroxo dicobalt(III) sulfate had been obtained) was strongly cooled and 35 ml of concentrated hydrochloric acid was slowly added within the space of 10 minutes. After a short time a green salt precipitated, while the remaining liquid was violet colored. The green salt was removed after about 1/2 hour. Yield: 1 gram. The insolubility of the sulfate was used as the basis for the [141]

first purification step. 12 g of green chloride were dissolved in 360 ml of water and the solution was acidified by adding acetic acid and then filtered; 20 g of sodium sulfate, $Na_2SO_4 \cdot 10H_2O$, dissolved in 60 ml of water was added a bit at a time. The sulfate precipitated nearly quantitatively after a short time in the form of small crystals and was removed from the mother liquor. This sulfate, which was still not pure, served as the starting material for the salt described below.

A. Conversion of the sulfate into the chloride

Twenty-four g of sulfate are ground into a thin suspension with about an equal amount of ammonium chloride and the reaction product removed with a Büchner funnel. This whole operation is repeated three or four times. The color of the chloride prepared in this way is dark olive-green. 2 g of this product are dissolved in 80 ml of weak acetic acid solution and 2 g of ammonium chloride are added to the filtered solution. A dark green chloride very quickly precipitates out and is suction filtered from the solution. Yield: 1.2-1.5 g. In order not to lose too much material, the mother liquor can be treated with concentrated hydrochloric acid and cooled to give a further yield of crystalline chloride.

B. Chloride:



Two g of the green chloride are covered with 1 ml of concentrated ammonia and the mixture is then diluted with 80-100 ml of cold water. The deep brown solution is quickly filtered and cooled and ammonium chloride is added with stirring, giving a precipitate of beautifully crystallized, lustrous greenish brown crystals of the salt. After about 20 minutes the salt is removed by suction filtration and washed with alcohol and ether. Some starting material may be recovered by treating the mother liquor with concentrated hydrochloric acid. [142]

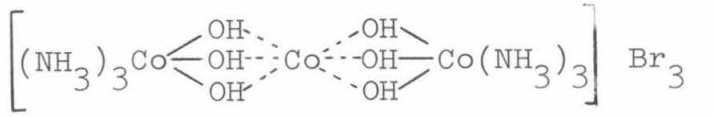
I. 0.1106 g gave 16.2 ml Nitrogen at 22° and 727 mm pressure
0.1000 g gave 0.0808 g AgCl

II. 0.1004 g gave 0.0864 g $CoSO_4$
0.1070 g gave 15 ml Nitrogen at 20° and 721 mm pressure
0.1006 g gave 0.0800 g AgCl

	calc. for $Co_3N_6O_6H_{21}Cl_3 \cdot 3H_2O$	found	
Co	32.6%	--- %	32.74%
N	15.5	16.21	15.91
Cl	19.6	19.97	19.66

The chloride is easily dissolved in water, giving an intensively yellow-brown solution.

C. Bromide:



Two g of green chloride are covered with 1 ml of concentrated ammonia, 80 ml of water are added and the solution is quickly filtered. The brown solution is treated with ammonium bromide and the precipitation of the bromide is speeded up by frequent agitation of the solution. The salt precipitates in small brown crystalline flakes, which are filtered off and washed with alcohol and ether. Yield: 1.2-1.5 g.

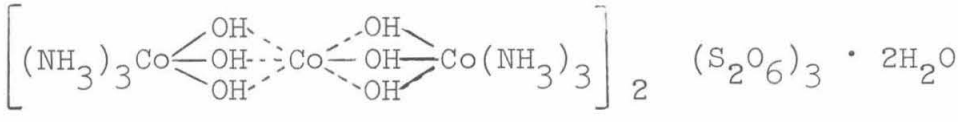
0.1014 g gave 0.0712 g $CoSO_4$

0.1006 g gave 12.6 ml Nitrogen at 21° and 722 mm pressure

	calc. for $Co_3N_6O_6H_{21}Br_3$	found
Co	26.2%	26.71%
N	12.4	13.82

The bromide is soluble in water, forming solutions having an intensive brown color.

D. Dithionate: [143]



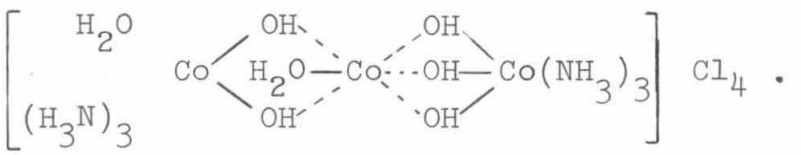
One g of green chloride is dissolved in water and sodium dithionate is added to the filtered solution. The dithionate precipitates out as brown crystals; it is almost insoluble in water.

0.1018 g gave 0.0760 g $CoSO_4$

0.1196 g gave 15.4 ml Nitrogen at 24° and 717 mm pressure

	calc. for $(Co_3N_6O_6H_{21})_2(S_2O_6)_3 \cdot 1H_2O$	found
Co	28.4%	28.4%
N	13.3	13.96

XXXIX. Diaquohexammine-penta-μ-hydroxo tricobalt(III) chloride



Cl_4 .

It is very easy to cleave one hydroxo bridge in the hexa-μ-hydroxo salts just described. When solutions of these salts are treated with mineral acids, green salts are obtained which correspond to the green chloride that was used as the starting material. These salts contain one anion more than the hexa-μ-hydroxo salts.

At this time we have only investigated the chloride. It is obtained from the cold solutions of any of the hexammine-hexa-μ-hydroxo tricobalt salts by precipitation with cold concentrated hydrochloric acid. Whether or not there is one chloride that is not ionically bound has not yet been established.

0.1006 g gave 0.0766 g $CoSO_4$

0.1016 g gave 0.0948 g AgCl

	calc. for $Co_3N_6O_7H_{17}Cl_4 \cdot 4H_2O$	found
Co	28.8%	28.99%
Cl	23.1	23.08

The green chloride dissolves very easily in water, forming a greenish-brown solution from which it may be reprecipitated [144] in the form of an intensively green crystalline powder by adding hydrochloric acid.

To my assistants, Mssrs. A. Grün, E. Bindschedler, G. Jautsch, O. de Vries, A. Schaarschmidt, Aeg. Tschudi, M. Feinberg, E. Scholze and Miss M. Grigorieff, I give my deepest thanks for their diligent assistance.